

**SOUTHERN CALIFORNIA AIR QUALITY STUDY:  
PEROXYACETYL NITRATE (PAN) MEASUREMENTS**

Agreement A6-099-32

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## EXECUTIVE SUMMARY

As part of the Southern California Air Quality Study (SCAQS), Daniel Grosjean and Associates, Inc. (DGA) has carried out measurements of ambient levels of peroxyacetyl nitrate (PAN) in the South Coast Air Basin (SCAB). PAN is a mutagen, a strong eye irritant, and a phytotoxic compound. PAN has no known direct sources. Like ozone, PAN is formed in-situ in the atmosphere as a product of hydrocarbon-NO<sub>x</sub> reactions. PAN is a major "carrier" for transport of atmospheric nitrogen on a regional scale. It is now recognized that PAN is of major importance (along with ozone) when evaluating the performance of air quality computer kinetic models.

As part of the SCAQS field measurements, PAN was measured simultaneously at nine (June and July 1987), seven (August and September 1987) and five locations (November and December 1987) as well as on board the two SCAQS aircraft. Ground-level measurements of PAN were carried out by electron capture gas chromatography (EC-GC). Calibration involved two methods, NO<sub>x</sub> chemiluminescence and liquid chromatography analysis of the PAN alkaline decomposition products. The latter method was also employed to measure PAN aloft.

Short, informal comparisons were carried out in the field during SCAQS. These limited studies suggest substantial differences between the EC-GC method and two variations of the luminol method. A more comprehensive comparison was carried out at the EPA laboratory in North Carolina. This study indicated good agreement between three PAN calibration methods, i.e. infrared spectroscopy, NO<sub>x</sub> chemiluminescence, and alkaline hydrolysis. Examination of a limited subset of ambient PAN data indicated that the corresponding measurement methods, both involving EC-GC, yielded ambient PAN data that were within 25% of each other, with good tracking of the PAN diurnal variations. As PAN measurements and the corresponding calibrations are by no means of a routine nature and are performed only by a small number of research groups, the 25% difference in reported ambient PAN concentrations appears reasonable and probably reflects the current state of measurements capabilities among laboratories that are proficient at measuring PAN by EC-GC.

A search for methyl nitrate, CH<sub>3</sub>ONO<sub>2</sub>, was also carried out. If present in ambient air, methyl nitrate would be recorded along with PAN under our EC-GC conditions. Methyl nitrate was synthesized, and response vs. concentration calibration curves were constructed using two methods, EC-GC and NO<sub>x</sub> chemiluminescence. Retention times of methyl nitrate and PAN were established for all field instruments. Interferences from a number of chlorinated hydrocarbons were examined in detail. A search of the some 3,500

chromatograms acquired during SCAQS yielded only seven possible observations of methyl nitrate at concentrations exceeding our detection limit of 0.2 ppb. Thus, methyl nitrate was not abundant in the SCAB atmosphere during SCAQS.

While PAN has long been observed in Southern California air, our study yielded for the first time information on the spatial and seasonal variations of PAN in the South Coast Air Basin. The highest PAN concentration during SCAQS, 30 ppb, was recorded at the Claremont site. Summertime levels of PAN exhibited a strong increase from coastal to inland locations (PAN levels at the "control" site, San Nicolas Island, were  $< 1$  ppb), and a corresponding shift in daily maxima from mid-day at coastal sites to late afternoon inland. Thus, spatial variations of PAN during the summer were consistent with considerations of photochemical production during transport. In contrast, levels of PAN during the fall phase of SCAQS were high at the coastal locations, e.g. 13-19 ppb at all five winter SCAQS sites on December 3, 1987. PAN concentrations aloft were up to 30 ppb and were comparable to (and often higher than) those measured at ground level.

## 1. INTRODUCTION AND PROJECT SCOPE

Peroxyacetyl nitrate (PAN,  $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ ) is a major product of photochemical reactions involving hydrocarbons and oxides of nitrogen in the atmosphere. PAN is an eye irritant, a mutagen, and a phytotoxic compound. Much of the  $\text{NO}_x$  emitted in urban air is converted to either PAN or nitric acid. Since nitric acid is rapidly removed from the atmosphere by dry and wet deposition, PAN is the major vehicle ("reservoir") for long range transport of nitrogen on a regional scale. The atmospheric persistence of PAN is limited by its thermal decomposition (which increases rapidly with increasing temperature) and by its reaction with emitted nitric oxide.

In addition to its key role as a  $\text{NO}_x$ -hydrocarbon reaction product, PAN has been investigated as a nighttime source of OH radicals and as an interferent in  $\text{NO}_2$  measurements by chemiluminescence. PAN is also an important parameter in the performance evaluation of atmospheric chemistry computer kinetic models.

In spite of its importance, PAN is not monitored as part of federal, state or county air pollution surveillance networks. Measurements of PAN in the South Coast Air Basin (SCAB) have been carried out in a research mode for over twenty years (Stephens 1969, Taylor 1969). Ambient levels of PAN in excess of 40-50 ppb have been recorded during severe smog episodes (Grosjean 1983, 1984 and references therein).

To our knowledge, PAN measurements to date have involved mostly short-term, intensive studies carried out at only one location. Virtually no information is available regarding spatial and seasonal variations of PAN in the SCAB atmosphere. The Southern California Air Quality Study (SCAQS) provided an opportunity to investigate these variations by carrying out simultaneous measurements of PAN at up to nine Southern California locations. These measurements were carried out during both summer 1987 and fall 1987 phases of SCAQS. They were complemented by a number of PAN interlaboratory comparison studies carried out both in the field and under laboratory conditions. As part of these studies, methyl nitrate, another nitrogenous pollutant, was also investigated in detail.

Accordingly, this report is organized in several major sections as follows. The first part describes our sampling and analytical methods, calibration procedures, field operations, and field and laboratory intercomparison studies. Results for methyl nitrate are also included, along with a brief discussion of the spatial and seasonal variations in PAN concentrations. Standard operating procedures and detailed error analysis are given in Appendices A and B, respectively. Individual data points for ground-level and aircraft PAN measurements are compiled in Appendix C.

## **2. EXPERIMENTAL METHODS**

Two methods were employed for the determination of ambient levels of PAN during SCAQS. Ground-level measurements were carried out using automated electron capture gas chromatographs operated on-site. Aircraft measurements were carried out by sampling air on alkaline traps and subsequently analyzing these samples for the alkaline decomposition products of PAN, i.e. acetate and nitrite, using liquid chromatography with ultraviolet detection.

### **2.1 Electron capture gas chromatography**

#### **2.1.1 Introduction**

Our PAN analyzers include six major components: a gas chromatograph, an electron capture detector (ECD), an integrator, a time clock, a cylinder of nitrogen (carrier gas) and a sampling pump. Ambient air samples are automatically injected every hour (every 30 min. at the Azusa site) using a 3 mL sampling loop.

#### **2.1.2 Gas chromatograph**

SRI model 8610 gas chromatographs equipped with Valco model 140-BN electron capture detectors (5 mCurie  $^{63}\text{Ni}$  foil) were used at all sites. The detectors were operated in a constant current variable frequency pulsed mode. Oven and detector temperatures were maintained at 60°C. Union Carbide ultra high purity nitrogen was used as the carrier gas. Table 1 lists the various columns used in the gas chromatographs to separate PAN from the other components in air, as well as the corresponding PAN retention times.

#### **2.1.3 Air sampling configuration**

The air sampling line consisted of: a 25 mm diameter, 1.2 micron pore size Teflon filter housed in a Nuclepore filter holder, a length of 1/4 inch diameter Teflon tubing leading to the gas chromatograph, a 3 cm<sup>3</sup> stainless steel sampling loop housed in the gas chromatograph oven and a modified Hagen Optima pump. Air was continuously pumped through the Teflon sampling line at flows of 0.2 to 0.5 lit. min<sup>-1</sup>. While the instrument was in the load mode, 10 minutes every hour, air was pumped through the stainless steel loop. When the gas chromatograph was switched to the injection mode, the 3 cm<sup>3</sup> air sample was injected into the column with carrier gas and the air passing through the Teflon sampling line bypassed the sampling loop.

**TABLE 1. GC COLUMNS EMPLOYED FOR PAN ANALYSIS DURING SCAQS**

Material & Support	Length, cm	Approximate PAN Retention Time, minutes	Column Type
10% Carbowax 400 on Chromosorb P, 60/80 mesh, AW - DMCS treated in 1/8" Teflon	90	$12 \pm 2$	"short"
Same as above	180	$27 \pm 5$	"long"
Same as above	132	$15 \pm 2$	"medium"
Same as above	50	$12 \pm 1$	"mini"
Same phase as above in 1/8" diameter Teflon lined stainless steel	180	$19 \pm 1$	"T-SS"
10% Carbowax 400 on Chromosorb W, 60/80 mesh AW-DMCS treated in 1/8" diameter Teflon	180	$10 \pm 1$	"long, Chrom W"

#### **2.1.4 GC Output**

The output of the detector is directed to a Hitachi D-2000 electronic integrator and recorded as a chromatogram. The chromatogram includes several peaks, one of which is PAN. A typical field chromatogram is shown in Figure 1 where PAN has a retention time of 8.3 min. PAN is quantitated by measuring the peak height or area and relating it to a calibration factor determined when a known concentration of PAN is injected into the gas chromatograph, see Section 4.1 for details.

#### **2.1.5 Reproducibility**

Reproducibility was tested in the laboratory by successive injections, over a 18-hour period, of a mixture of PAN prepared in a 3.5 m<sup>3</sup> Teflon chamber. The PAN peak heights and areas were found to be reproducible within  $\pm 2\%$  and  $\pm 1\%$ , respectively. Reproducibility was also tested in the field using the constant PAN output of a photochemical flow reactor. Peak heights and areas were reproducible, over 16-hour periods, within  $\pm 2.1\%$  in Claremont (long column) and  $\pm 4.9\%$  in Azusa (medium column).

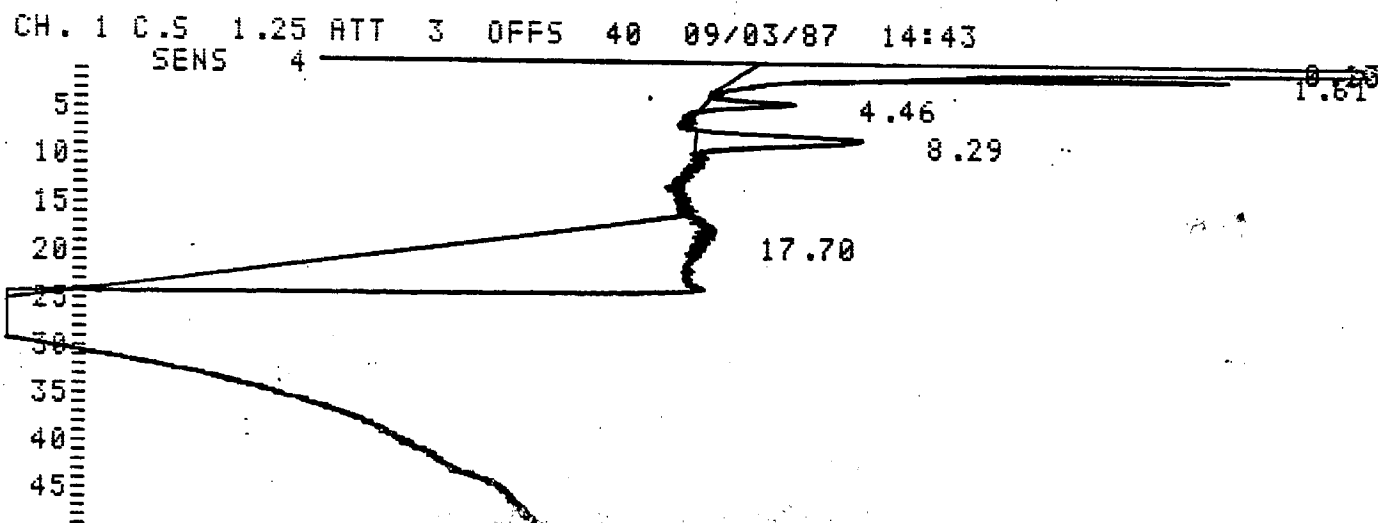
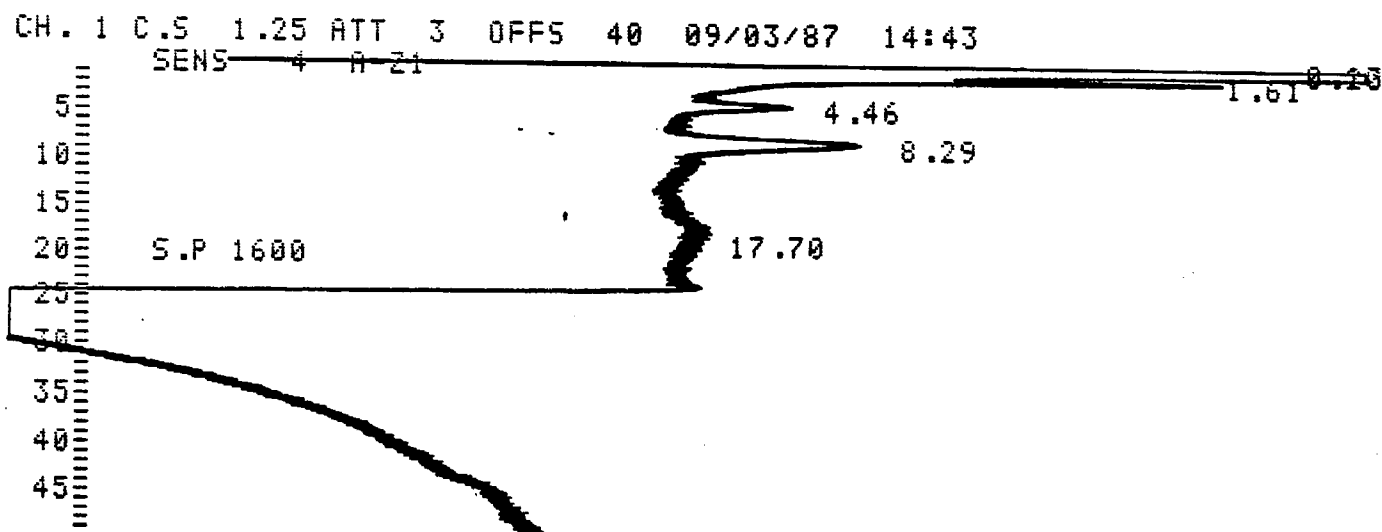
#### **2.1.6 Detection limits**

PAN peak heights were used to calculate the PAN concentration from all field chromatograms. Under ideal conditions peak heights of 1 mm or more could be measured. The analytical detection limit for each gas chromatograph is defined as the calibration factor in ppbv/mm times 1 mm. These detection limits varied by site and time period as is shown in Table 2. In most cases the analytical detection limits ranged from 0.2 to 0.8 ppbv. We conservatively set the field detection limit for these instruments to be 1 ppb. As is described in more detail in Section 3.3, operating conditions in the field were less than ideal, and the detection limit was often limited by baseline noise, baseline stability and other problems. In those cases the actual detection limit has been calculated for each site and time period, and has been indicated in the Data Report (Appendix C) when appropriate.

### **2.2 Alkaline trap sampling and liquid chromatography analysis**

Aircraft samples were collected using Teflon-alkaline filter packs housed in a dual 47 mm diameter filter holder. The upstream Teflon filter (Sartorius, 1.2  $\mu$ m pore size) removed particulate matter. The downstream filter was a Gelman AE glass filter impregnated with a solution of potassium hydroxide in methanol. After sampling, the

FIGURE 1. TYPICAL FIELD CHROMATOGRAM



CLAREMONT

D-2000

09/03/87 14:43

SAMPLE: PAN ANALYSIS TAG: 49 CH: 1

FILE: 1 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	0.13	3295468	65.699	BU
2	0.20	62472	1.245	TBB
3	1.61	32748	0.652	TBB
4	4.46	23276	0.464	BB
5	8.29	79496	1.584	BB
6	17.70	1522507	30.353	BB

TOTAL

5015967 100.000

PEAK REJ : 2000

**TABLE 2. PAN ANALYTICAL DETECTION LIMITS**

TIME PERIOD				SCAQS SITE	DETECTION LIMIT, ppb
Start		Stop			
Date (1987)	Time (PST)	Date (1987)	Time (PST)		
6/19	0:56	6/26	1:24	Anaheim	0.7
7/12	20:33	7/15	23:33	Anaheim	0.1
8/26	21:06	9/4	0:03	Anaheim	0.2
11/11	0:39	12/11	23:34	Anaheim	0.4
6/18	10:12	9/3	21:07	Azusa	0.5
6/19		6/26	1:16	Burbank	0.8
7/12	22:40	9/3	23:38	Burbank	0.6
11/11	0:31	12/11	23:26	Burbank	0.4
6/19		7/15	23:57	Claremont	0.7
8/27	0:03	9/1	12:00	Claremont	0.2
9/1	19:40	9/10	15:42	Claremont	0.2
6/19		6/26	0:46	Hawthorne	0.8
7/13	0:49	7/13	18:49	Hawthorne	0.4
7/13	20:44	7/15	23:45	Hawthorne	0.8
11/11		11/14		Hawthorne	0.5
11/14		12/12		Hawthorne	0.3
6/19		7/13	13:44	Long Beach	1.0
7/13	16:12	9/4	1:22	Long Beach	0.6
11/11	8:01	12/11	23:16	Long Beach	0.6
6/19		7/16	0:16	Los Angeles	0.7
8/27	1:02	12/11	21:31	Los Angeles	0.3
6/19		7/16	1:42	Rubidoux	1.8
8/26	20:15	9/4	0:33	Rubidoux	0.7
7/13	0:44	7/16	0:45	San Nicolas	0.5



alkaline filters were promptly placed in individual glass vials sealed with Teflon-lined screwcaps. The vials contained 10 mL of deionized water and 40 microliters of chloroform added as a biocide. The addition of a biocide is critical to the stability of the samples, even upon storage in the dark at refrigerator temperature.

PAN decomposes in alkaline medium to acetate and nitrite, which were determined by liquid chromatography with ultraviolet detection as is described in detail elsewhere (Grosjean et al., 1988). The method involves separation on a size exclusion resin column (Hamilton PRP-X-300) with dilute sulfuric acid eluent (5mM H<sub>2</sub>SO<sub>4</sub>, eluent flow rate 1 mL per minute) and uv detection at a wavelength of 210 nm. Calibration involved the use of external standards, i.e. dilute solutions of sodium acetate and sodium nitrite in deionized water. The collection efficiency of the alkaline traps at flow rates relevant to this work has been previously established (Grosjean, 1988), and is  $\geq 0.97$  for acetate and  $\geq 0.98$  for nitrite. Analytical detection limits (100  $\mu$ L injections) are 34 and 12 nanograms for acetate and nitrite, respectively. Multiple injections of standard solutions yielded relative standard deviations (RSD) of 3.0% for both acetate and nitrite. Replicate analysis of field samples yielded RSDs of 8.5% for acetate (range = 4-12%, 15 sets of replicates) and 8.3% for nitrite (range = 6-11%, 13 sets of replicates).

### **3. FIELD OPERATIONS**

#### **3.1 Sampling locations**

PAN analyzers were located at nine and five ground sites during the summer and fall sampling phases of SCAQS, respectively. In June and July, PAN was measured at the Anaheim, Azusa, Burbank, Claremont, Hawthorne, Long Beach, Los Angeles, Rubidoux and San Nicolas Island sites. In August and September, PAN measurements were discontinued in Hawthorne and San Nicolas Island. In November and December, PAN was measured at Anaheim, Burbank, Hawthorne, Los Angeles and Long Beach.

All locations except Claremont and Long Beach were SCAQMD air monitoring stations. In Long Beach, the PAN analyzer was located in the ARB trailer with the sample inlet approximately thirty feet from the sampling platform. In Claremont, the PAN analyzer was in the ARB Headquarters trailer with the sample inlet about twenty feet from the sampling platform. The instrument was then moved on September 1 to Seavers Hall on the Pomona College Campus, approximately one-half mile from its initial location.

All PAN analyzers had their own 1/4 inch diameter Teflon sampling lines. Sampling line lengths, air flow rates and the corresponding residence times are listed in Table 3.

A number of tests were carried out to investigate the possible loss of PAN in the sampling lines. Results of these tests are summarized in Table 4 and indicate no measurable loss of PAN in lines of up to 145 ft. Relevant data from other SCAQS investigators are also listed in Table 4. During SCAQS, all sampling lines were outfitted with Teflon filters which minimized line contamination by gases and particles that may act as a sink for PAN, e.g. alkaline particles. Tests carried out with and without Teflon filters indicated no measurable loss of PAN on the Teflon filters.

#### **3.2 Field activities**

An electron capture gas chromatograph is a very sensitive instrument. It requires four to five hours to stabilize after start-up. Thus, it was necessary to have all instruments running continuously during any period a GO day might be called. Field activities included: the set up of the PAN analyzers, verification of the operational status of the instruments, troubleshooting and on-site repair when necessary,

**TABLE 3. SAMPLING LINES DIMENSIONS, SAMPLING FLOW RATES AND SAMPLE LINE RESIDENCE TIMES**

Site	Summer /fall	Sample line length, m	Sample line i.d., mm	Sampling flow rate, ml/min.	Sample line residence time, min
Anaheim	S	5.8 ± 0.1	4.8	257 ± 12	0.41
Anaheim	F	5.8 ± 0.1	4.8	330 ± 12	0.32
Azusa	S	6.0 ± 0.3	6.4	300 ± 12	0.64
Burbank	S	4.0 ± 0.1	4.8	247 ± 12	0.29
Burbank	F	4.0 ± 0.1	4.8	389 ± 12	0.19
Claremont	S	5.2 ± 0.3	6.4	>200	<0.84
Hawthorne	S	7.0 ± 0.5	6.4	257 ± 12	0.88
Hawthorne	F	7.0 ± 0.2	6.4	260 ± 12	0.87
Long Beach	S	5.8 ± 0.1	4.8	440 ± 12	0.24
Long Beach	F	5.8 ± 0.1	4.8	319 ± 12	0.33
Los Angeles	S	7.0 ± 0.3	4.8	194 ± 12	0.65
Los Angeles	F	7.0 ± 0.3	4.8	425 ± 12	0.30
Rubidoux	S	3.5 ± 0.5	6.4	260 ± 12	0.43
San Nicolas	S	12.2 ± 0.6	4.8	>200	<1.10
Median values		6.3		291 ± 80	0.54

**TABLE 4. SUMMARY OF SAMPLING LINE LOSS TESTS**

Group	Location and date	T( C)	Teflon sampling line dimensions	PAN, ppb (a)	PAN loss
DGA(b,c)	Getty Museum, 9/88 Malibu, CA	22	1/4 inch x 50 ft	3.3	no loss
			1/4 x 120 ft	3.3	
DGA	Southwest Museum, 10/88 Los Angeles, CA	27	1/4 x 18	7.7	10% in 58 ft
			1/4 x 76	7.6	
DGA	DGA lab, Ventura, CA, 11/88	20	1/4 x 25	12.3	no loss in up to 145 ft
			1/4 x 65	12.3	
			1/4 x 145	12.8	
			1/4 x 30, new tubing	13.2	
U. Denver	Azusa SCAQS site, 6/87	-	no line	33.6	5.4% 12.2%
			1/4 x 8	31.8	
			1/4 x 28	29.5	
GM	Los Angeles SCAQS site, 6/87	-	1/8 x 40	-	10%

(a) DGA PAN data are averages of at least 3 measurements

(b) PAN measured by EC-GC (DGA, GM) or with luminol method (U. Denver)

(c) DGA sampling flow rates were in the range of those listed in Table 3; that of GM was 0.2 L/min.

coordination of the delivery of nitrogen cylinders to all sites, and the periodical replacement of nitrogen carrier gas cylinders. Details of the operating procedures are given in Appendix A.

Duties of Aerovironment personnel on GO days included switching the PAN analyzer from the standby to the data recording mode, checking the nitrogen cylinder regulator pressure, recording the baseline voltage and making sure the chart paper did not jam. Instructions for the AV personnel were posted near the PAN analyzers and appear in Appendix A (Standby Procedure for DGA PAN Analyzers, PAN Analyzer Short Daily checklist and PAN Analyzer Baseline Voltage Log Sheet). At the end of a GO day, AV staff would switch the PAN analyzer to the standby mode. All problems and emergencies were reported to DGA, day or night.

The gas chromatographs were checked by DGA personnel every two to three days in-between GO days and every day during GO days. A PAN analyzer Long Daily Checklist, see Appendix A, was filled out and the results were reported to the DGA project manager. Other tasks included: changing chart paper and Teflon filters, verification of the operational status of the air conditioning, and making sure that AV staff had switched the instruments to the data recording mode on the evening of a GO Day. With up to nine PAN analyzers running simultaneously, it was often necessary to proceed with on-site maintenance and instrument optimization at up to three sites on any given day.

### **3.3 Difficulties in field operations**

The early phase of the summer field campaign was fraught with difficulties. Of these, many were of a logistical nature inherent to the size and scope of the SCAQS field operations.

Instrument set-up was hampered at all sites by lack of space, wrong space assignment, inability to access the site (e.g. wrong keys), delays and/or errors in delivery of nitrogen gas cylinders, inability to set-up sampling lines, etc. Two of our instruments were actually displaced (each time with damage), one of them on a GO Day. Delays and conflicting information regarding delivery of nitrogen on San Nicolas Island resulted in two unnecessary trips by DGA staff; measurements could only be initiated after missing three GO days.

Instrument performance was hampered by many factors which affected instrument baseline stability, detector response, or both, and/or caused severe problems including detector contamination, interferences, and

sample integrity. Major problems included "fumigation" of our electron capture detectors by Freon 12 (e.g. calibration of nephelometers located next to our instruments at most sites, or large release from the mobile lab of a SCAQS participant in Claremont), and contamination by nitric oxide (which reacts rapidly with PAN) resulting from calibration of nearby  $\text{NO}_x$  and  $\text{O}_3$  analyzers and from the high nitric oxide output (6 ppm) of the peroxide instruments located next to our instruments at nearly all sites. On-site calibrations were hampered by lack of space and/or power needed for correct operation of the PAN generator, and could not be carried out on GO days.

These and other difficulties, all recorded in a detailed "SCAQS Journal" which is available upon request, resulted in the early phase of the field study being carried out under less than adequate conditions. While remedial measures were promptly implemented, we feel that our measurements during the early phase of SCAQS were of limited reliability at several of the sites. At the completion of the June-July phase of the summer measurements, all instruments were brought back to the DGA laboratory. They were outfitted with a new microchip and regulation device that allowed for better temperature control, increased baseline stability, and therefore better detection limits. New columns were installed and the modified instruments were tested and calibrated. These hardware improvements, while not needed for measuring PAN under "normal" conditions, were critical to obtain satisfactory instrument performance during SCAQS. All instruments responded well to hardware improvements, were fully re-calibrated, and were re-deployed in the field prior to the second phase of the summer study.

## 4. CALIBRATION PROCEDURES

### 4.1 Peroxyacetyl nitrate

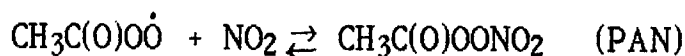
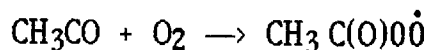
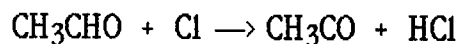
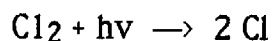
#### 4.1.1 Overview

PAN calibrations involved the following three steps:

- a reference gas chromatograph (GC) was calibrated using a stable source of PAN. As injections were made on the PAN instrument, the concentration of PAN produced by the source was determined by two independent methods, (a) NO<sub>x</sub> chemiluminescence and (b) liquid chromatography determination of acetate following PAN alkaline hydrolysis. Calibration curves, i.e. peak height vs. concentration and peak area vs. concentration, were constructed using several dilutions of the PAN source. The slopes of these calibration curves, i.e. calibration factors, (peak height (mm) per ppb and peak area (counts) per ppb), were determined by regression analysis of the experimental data.
- each field instrument was compared to the reference GC by carrying out side-by-side measurements of PAN from one or more dilutions of the PAN source. A calibration factor for each field instrument could thus be obtained by multiplying the calibration factor of the reference GC and the relative response of that instrument to that of the reference GC.
- the retention time of PAN on each field instrument was verified in the field by bringing to the site a source of PAN (portable photochemical flow reactor) and by taking samples from that source with the field instrument at each site (see Appendix A).

#### 4.1.2 PAN generator

A stable source of PAN was produced in a photochemical reactor (Grosjean et al, 1984) by photolysis of molecular chlorine in the presence of acetaldehyde and nitrogen dioxide. The reaction sequence for PAN production is:



The output of the PAN generator is stable within 2% (peak area) and 3% (peak height) when measured by successive injections every 30 minutes during a 15-hour period.

#### **4.1.3 Alternative source of PAN**

All calibrations were carried out using the PAN generator described in the preceding section. Another method to prepare ppb levels of PAN was used to (a) confirm PAN production and retention times by an independent method, (b) carry out instrument stability tests, see Section 2.1.5, and (c) carry out sampling line loss tests, see Section 3.1 and Table 4. This second method involved sunlight irradiation, in a 3.5 m<sup>3</sup> all-Teflon chamber, of ~0.2 ppm of nitric oxide and ~2 ppm of the olefin, 2-methyl-2-butene, in purified air. Reactions of the olefin with ozone and with the OH radical rapidly produce acetaldehyde, which in turn reacts with OH to produce PAN according to the sequence of reactions given above (Section 4.1.2).

#### **4.1.4 PAN alkaline decomposition method**

The alkaline hydrolysis of PAN yields acetate and nitrite (Stephens, 1969). Alkaline-impregnated cartridges were collected on the full output of the PAN generator, typically 200-300 ppb. The cartridges were then eluted and analyzed for acetate by HPLC with ultraviolet detection. The step-by-step procedure is as follows:

- Establish that the PAN concentration obtained from the PAN generator is stable by making three injections on the PAN analyzer.
- Insert two impingers in series, each containing 10 ml of deionized water, between the PAN generator and the gas chromatograph. The flow rate through the impingers is controlled by the GC sampling line and is typically in the range of 300 ± 80 ml/min. Measure the flow rate through the impingers.
- Make successive injections on the PAN analyzer until a constant amount of PAN is removed by the water impingers. This usually takes one to two hours (2-4 injections).
- Collect an alkaline cartridge downstream of the water impingers. The sampling time is calculated from the acetate detection limit on the HPLC, the flowrate through the cartridge and the approximate PAN concentration.
- After collection of the alkaline cartridge verify that the PAN output of the generator is still the same by making at least two injections on the GC downstream of the water impingers.



- Elute the alkaline cartridge and analyze for acetate by HPLC with ultraviolet detection, see Section 2.2.

#### 4.1.5 NO<sub>x</sub> chemiluminescence method

Chemiluminescence NO<sub>x</sub> analyzers respond quantitatively to other nitrogenous compounds including PAN. Measurements of PAN from the generator output are thus possible, provided that the unreacted NO<sub>2</sub> is taken into account. The method involves the use of a chemiluminescent analyzer (e.g. Monitor Labs model 8840) and of an alkaline-impregnated cartridge as follows:

- insert an alkaline cartridge between the PAN generator and the GC, inject downstream onto the GC to verify that all of the PAN is retained on the cartridge.
- measure, using dilute mixtures of NO<sub>2</sub> in pure air, the amount of NO<sub>2</sub> that is also retained on the cartridge (20.2% for the conditions employed in our laboratory).
- measure by chemiluminescence the NO<sub>x</sub> concentrations upstream and downstream of the alkaline cartridge.
- calculate PAN = NO<sub>x</sub> (upstream) - 1.253 NO<sub>x</sub> (downstream)

The factor 1.253 corresponds to 20.2% NO<sub>2</sub> removal on the alkaline cartridge, i.e. NO<sub>2</sub> = 1/(1-0.202) NO<sub>x</sub> (downstream)

#### 4.1.6 Calibration factors for reference gas chromatograph

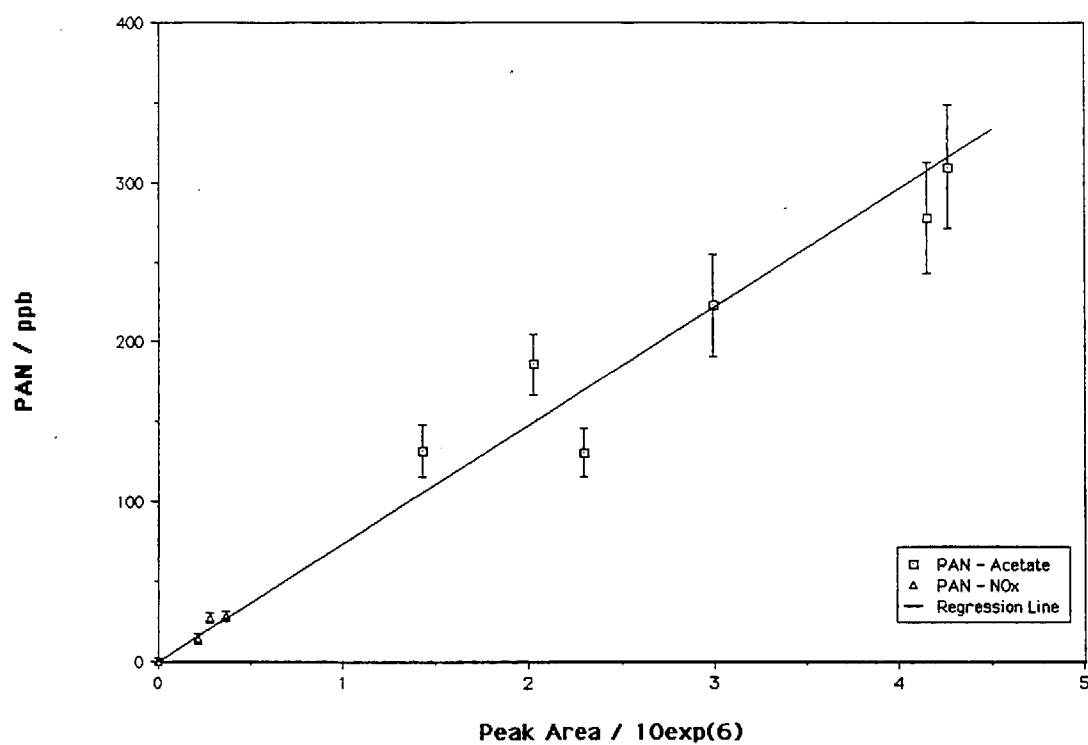
Plots of the PAN peak areas and PAN peak heights measured with the reference GC versus the corresponding PAN concentrations are shown in Figure 2. The triangles and boxes represent chemiluminescence and alkaline hydrolysis method data, respectively. Regression analysis of the experimental data (weighted least squares, forced through zero, see Appendix B for details) yields the following slopes, i.e. calibration factors:

Peak Area:  $7.414 \pm 0.314$  ppb per  $10^5$  area count,  $R = 0.983$

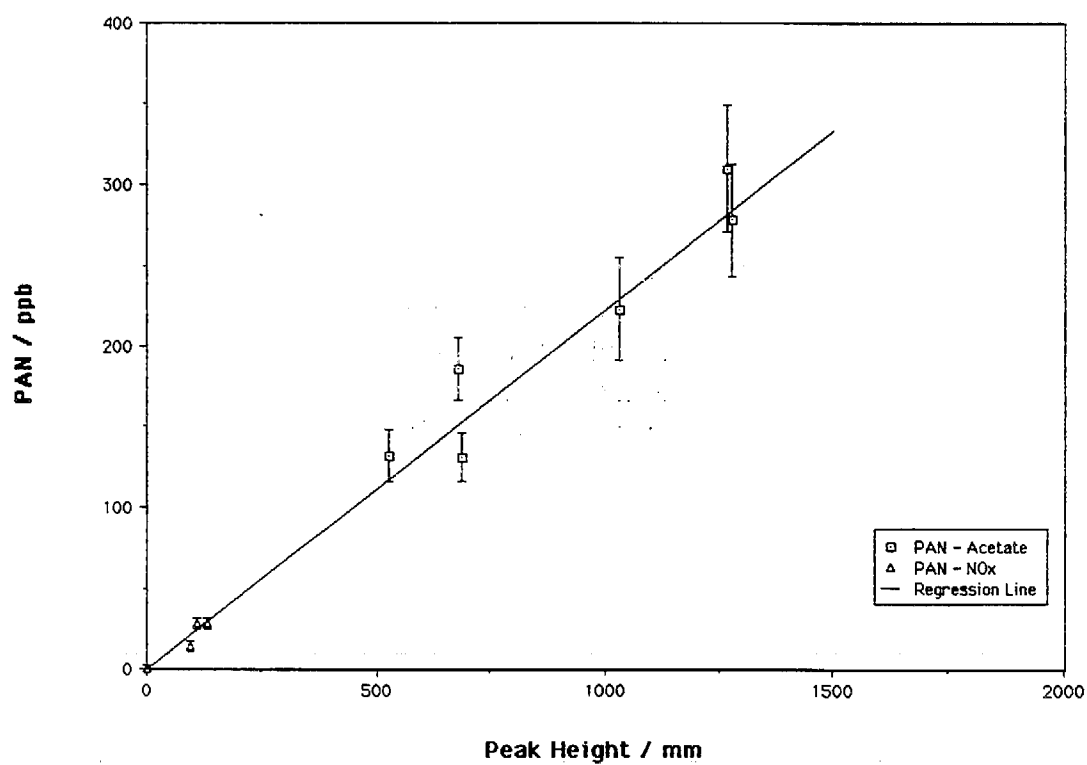
Peak Height:  $0.2224 \pm 0.0094$  ppb per mm,  $R = 0.988$

FIGURE 2. CALIBRATION DATA FOR REFERENCE GC

Peak Area Calibration Data for Reference GC



Peak Height Calibration Data for Reference GC



#### 4.1.7 Calibration of field instruments

All gas chromatographs used during SCAQS were calibrated by comparison with a single reference GC. Relative peak area response factors were calculated by dividing the PAN peak area for the field GC by that measured on the reference GC. Similarly, relative peak height response factors were calculated. Relative responses were measured at both high and low PAN concentrations. PAN concentrations measured with the reference GC are plotted in Figure 3 against those measured with all other gas chromatographs. The data indicate that the relative response factors are constant at both high and low PAN concentrations.

Peak area, R1, and peak height, R2, response factors for each GC are summarized in Table 5. They were calculated from 3-15 sets of side-by-side comparisons.

Calibration factors in units of ppbv/mm were calculated for each GC from the reference GC peak area and peak height calibration factors. Equation 4.1 was used to calculate the calibration factor,  $C_X$ , from the peak height response factor, R2:

$$\frac{1}{R2} \times C2 = C_X \quad (\text{Eq.4.1})$$

where C2, the reference GC calibration factor is 0.2224 ppb/mm. To calculate the calibration factor from the peak area response factor, R1, equation 4.2 was used:

$$\frac{1}{R1} \times A \times C1 = C_X \quad (\text{Eq.4.2})$$

where  $C1 = 7.414 \times 10^{-5}$  ppb/count and A is the PAN peak area divided by the peak height. The calibration factors derived from the reference GC peak area and peak height calibration appear in the last two columns of Table 5 and are plotted against each other in Figure 4. The two sets of calibration factors agreed in most cases. Calibration factors derived from equation 4.1. were used to report all SCAQS PAN data. The variable A introduces an additional uncertainty and makes calibration factors derived from equation 4.2 less accurate than those from equation 4.1. The calibration factors for each GC used during SCAQS and the applicable time periods appear in Table 6.

Figure 3  
CALIBRATION DATA FOR ALL FIELD INSTRUMENTS

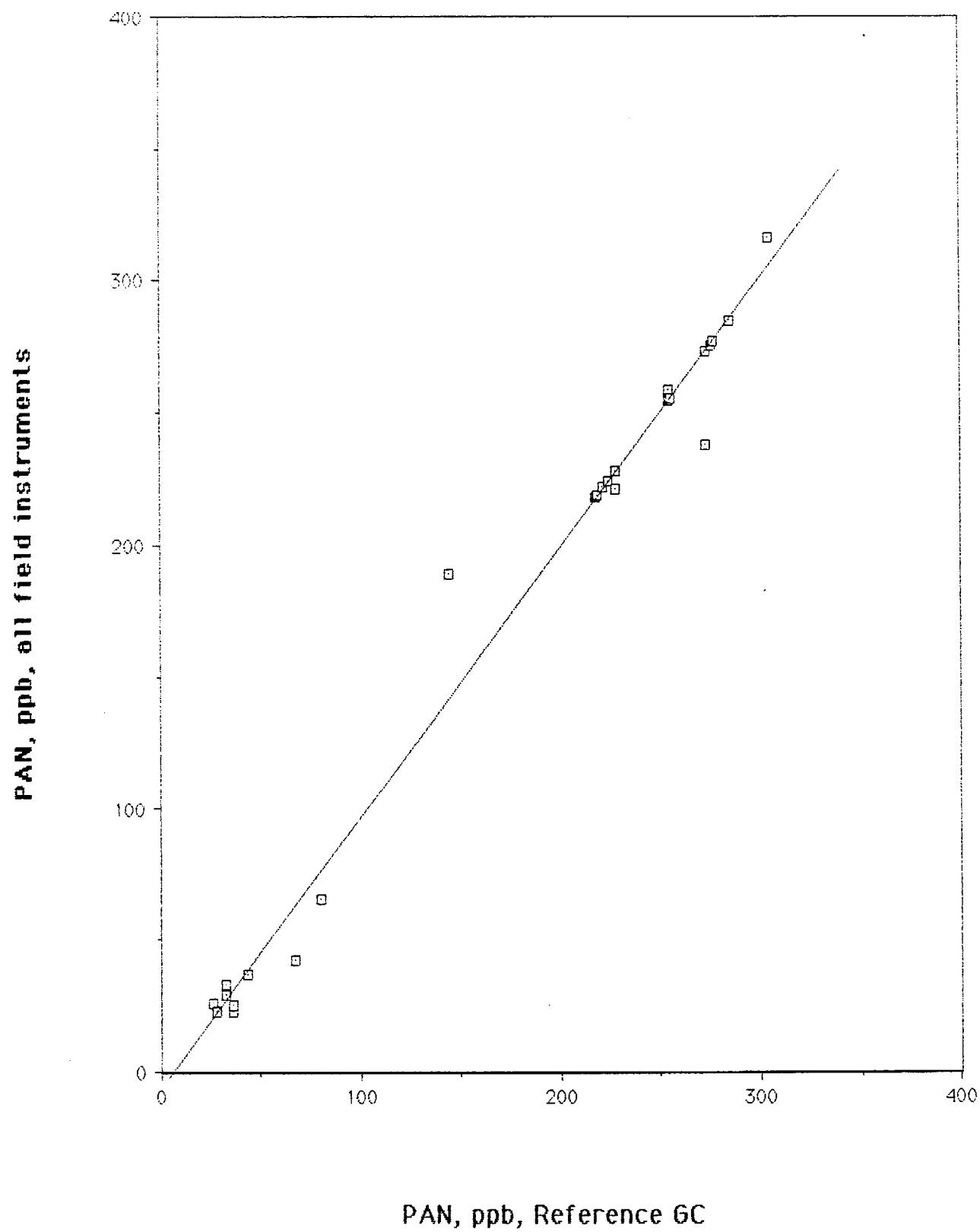


Figure 4. Peak Height and Peak Area Calibration Factors

### Peak Area vs Peak Height Calibration Factor Plot

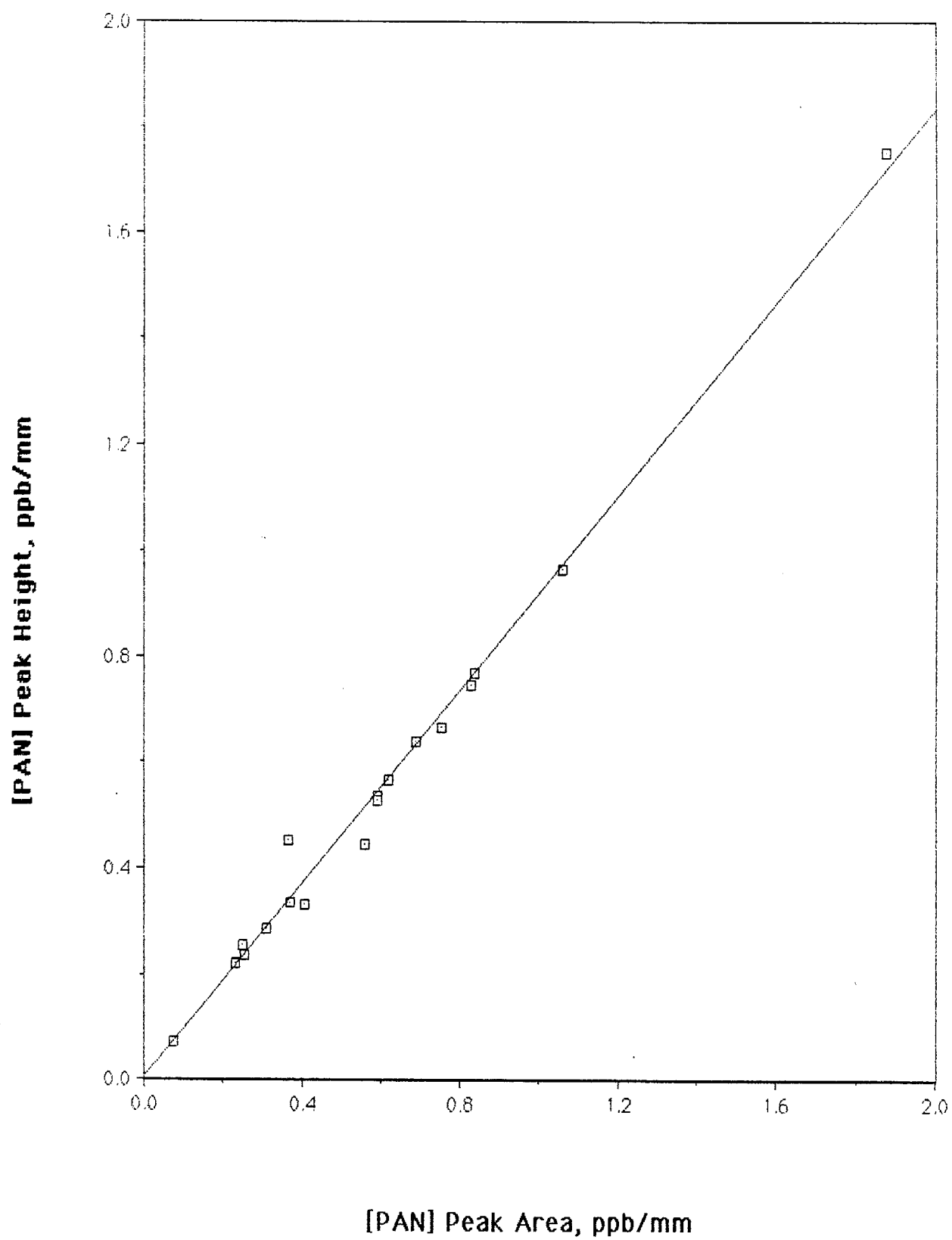


TABLE 5. SUMMARY OF RESPONSE FACTORS FOR FIELD INSTRUMENTS

GC	Comparison Month	Location	Column	Retention time, min.	Relative peak area		Relative peak height R2 = height/height Ref	Peak Area		PAN Calibration Factors	
					R1 = area/area REF			Peak Height, 1/1000 mm	Peak Area, ppb/mm	Peak Height, ppb/mm	
51	Oct	Claremont	short (a)	7	1.00(a)		1.00(a)	3.12	0.231	0.222	
51	Oct	Claremont	long	22	0.789			7.11(b)	0.668	0.615(c)	
51	Oct	Claremont	long	26.0						0.663(d)	
51	Oct	Claremont	short	9.2	1.216		0.937	4.18	0.255	0.237	
58	Oct	Los Angeles	long	28.1	0.853			8.56(b)	0.744	0.684(c)	
58	Oct	Los Angeles	short	11	1.078		0.774	4.49	0.309	0.287	
58	Oct	Los Angeles	short (e)	11.4	1.147		0.664	5.73	0.370	0.335	
52	Oct	Azusa	medium	15.2	0.846			5.91(f)	0.518	0.477(c)	
57	Oct	Rubidoux	long	32.2	0.303		0.127	7.67	1.877	1.751	
57	Oct	Rubidoux	short	12.5	0.474		0.333	4.80	0.751	0.668	
53	Oct	Long Beach	short	15.6	0.735		0.348	6.81	0.687	0.639	
53	Oct	Long Beach	long	30	0.605		0.231	8.63	1.058	0.963	
54	Oct	Burbank	long, Chrom W	10	0.68		0.391	5.70	0.621	0.569	
54	Oct	Burbank	long	33.4	0.825		0.289	9.31	0.837	0.770	
55	Oct	Anaheim	mini	12.6	1.564			5.08(f)	0.241	0.223(c)	
55	Oct	Anaheim	long	20.6	0.593			6.61	0.826	0.746	
55	Feb	Anaheim	T-SS	19	6.64			6.47	0.072	0.073	
59	Oct	San Nicolas Is.	long	26.4	0.888			7.07	0.590	0.536	
56	Oct	Hawthorne	long	27(g)	0.694			5.89	0.629(g)	0.818(g)	
56	Oct	Hawthorne	short	12 (g)	0.9			5.11	0.421(g)	0.363(g)	
51	Dec	DGA lab	short (a)	8.0 ± 1	1 (a)			nd	nd	0.222	
55	Dec	Anaheim	mini	12.3	1			7.52	0.558	0.445	
52	Dec	Hawthorne	medium	9	0.667			3.65	0.406	0.333	
57	Dec	Burbank	short	12	0.718			3.52	0.363	0.452	
54	Dec	Long Beach	long, Chrom W	8.9	0.641			5.12	0.592	0.528	
58	Jan	Los Angeles	short	9.8	1.18			4.00	0.251	0.255	

(a) Reference

(b) calculated from regression of retention time (vs. peak area/peak height) for all data

(c) calculated from regression of peak area (column 9) vs. peak height (column 10) PAN calibration factors

(d) calculated from the Claremont, long R.T. 22.0 data and data from a plot of peak height vs. retention time, see Appendix B

(e) Repeat after 5 days

(f) calculated directly from experimental data for that specific instrument; these values were within 2% (Anaheim, mini) and 6% (Azusa, medium) of those calculated from the regression, see footnote (b)

(g) Estimated from the mean value for identical columns

TABLE 6. SCAQS PAN CALIBRATION FACTORS

Location	Start		Stop		GC	Column	Calibration factor ppb/mm
	Date (1987)	Time	Date (1987)	Time			
Anaheim	6/19	0:56	6/26	1:24	55	long	0.746
Anaheim	7/12	20:33	7/15	23:33	55	T-SS	0.073
Anaheim	8/26	21:06	9/4	0:03	55	mini	0.223
Anaheim	11/11	0:39	12/11	23:34	55	mini	0.445
Azusa	6/18	10:12	9/3	21:07	52	medium	0.477
Burbank	6/19		6/26	1:16	54	long	0.770
Burbank	7/12	22:40	9/3	23:38	54	long, Chrom W	0.549(a)
Burbank	11/11	0:31	12/11	23:26	57	short	0.452
Claremont	6/19		7/14	18:26	51	long	0.663
Claremont	7/14	18:56	7/15	23:57	51	long	0.615
Claremont	8/27	0:03	9/1	12:00	51	short	0.237
Claremont	9/1	19:40	9/10	15:42	51	sea-short	0.222
Los Angeles	6/19		7/16	0:16	58	long	0.684
Los Angeles	8/27	1:02	12/11	21:31	58	short	0.292
Hawthorne	6/19		6/26	0:46	56	long	0.818
Hawthorne	7/13	0:49	7/13	18:49	56	short	0.363
Hawthorne	7/13	20:44	7/15	23:45	56	long	0.818
Hawthorne	11/11	0:03	11/14		52	medium	0.477
Hawthorne	11/14		12/12	0:34	52	medium	0.333
Long Beach	6/19		7/13	13:44	53	long	0.963
Long Beach	7/13	16:12	9/4	1:22	53	short	0.639
Long Beach	11/11	8:01	12/11	23:16	54	long, Chrom W	0.549 (a)
Rubidoux	6/19		7/16	1:42	57	long	1.751
Rubidoux	8/26	20:15	9/4	0:33	57	short	0.668
San Nicolas	7/13	0:44	7/16	0:45	59	long	0.536

(a) Average of summer and fall calibrations.

## 4.2 Methyl nitrate

Methyl nitrate was synthesized at DGA by mixing (15 ml conc.  $\text{H}_2\text{SO}_4$  + 15 ml  $\text{HNO}_3$ ) and (2.5 ml  $\text{H}_2\text{SO}_4$  + 7.5 ml  $\text{CH}_3\text{OH}$ ) at ice temperature. Methyl nitrate (oily layer) was separated and washed with 22% NaCl in water.

Methyl nitrate thus prepared was identified by recording its infrared spectrum at the EPA laboratory, see Section 5.1. Major absorption peaks were as follows:

1640	$\text{cm}^{-1}$	(assymetric - $\text{NO}_2$ stretch)
1290	$\text{cm}^{-1}$	(symmetric - $\text{NO}_2$ stretch)
800	$\text{cm}^{-1}$	(broad CO - N stretch)
750	$\text{cm}^{-1}$	( $\text{NO}_2$ bend)

The spectrum of the methyl nitrate prepared at DGA matched well that of a sample of methyl nitrate prepared independently by EPA, see Section 5.1.

The stability of methyl nitrate at ppb levels in pure air was investigated before calibrations were carried out. The results of five experiments carried out with ppb levels of  $\text{CH}_3\text{ONO}_2$  in pure air in a 3.5  $\text{m}^3$  Teflon chamber are summarized in Table 7. One of the experiments is illustrated in Figure 5. The overall stability is excellent ( $\pm 1.5\%$ ) and is a composite measure of the following parameters:  $\text{CH}_3\text{ONO}_2$  stability, stability of the measurement methods ( $\text{NO}_x$  chemiluminescence and EC-GC), and negligible loss to the walls of the Teflon chamber.

Calibrations using both EC-GC and  $\text{NO}_x$  chemiluminescence were carried out by successive dilution of ~250 ppb  $\text{CH}_3\text{ONO}_2$  in pure air using a 3.5  $\text{m}^3$  Teflon chamber (the matrix air was first checked for methyl nitrate contamination). A plot of chemiluminescent analyzer vs. electron capture detector response is shown in Figure 6. Non-linearity of this plot beyond 40 ppb raised a question whether our GC or  $\text{NO}_x$  analyzer have non-linear response to methyl nitrate. This question was answered by plotting  $\text{NO}_x$  analyzer and EC-GC responses versus dilution, see Figure 7. The data shown in Figure 7 suggest that the  $\text{NO}_x$  analyzer used in this study has a non-linear response to methyl nitrate above ~60 ppb. This is probably due to the decreased conversion efficiency of the catalytic converter at higher  $\text{CH}_3\text{ONO}_2$  concentrations.

Our detection limit for methyl nitrate, as calculated from the curve shown in Figure 6, is 0.2 ppb.



TABLE 7. METHYL NITRATE STABILITY STUDIES

Experiment No.	Initial concentration, ppb	Final concentration, ppb	Length of study, hrs.	No. of data points	Loss rate, ppb/hr.
1	$62 \pm 2$	$62 \pm 2$	10	10	$0 \pm 1.5\%$
2	$39 \pm 2$	$39 \pm 2$	17	18	$0 \pm 1.5\%$
3	$145 \pm 2$	$145 \pm 2$	8	8	$0 \pm 1.5\%$
4	$188 \pm 2$	$188 \pm 2$	10	10	$0 \pm 1.5\%$
5	$152 \pm 2$	$152 \pm 2$	10	10	$0 \pm 1.5\%$

Figure 5

# Methyl Nitrate Stability Experiment

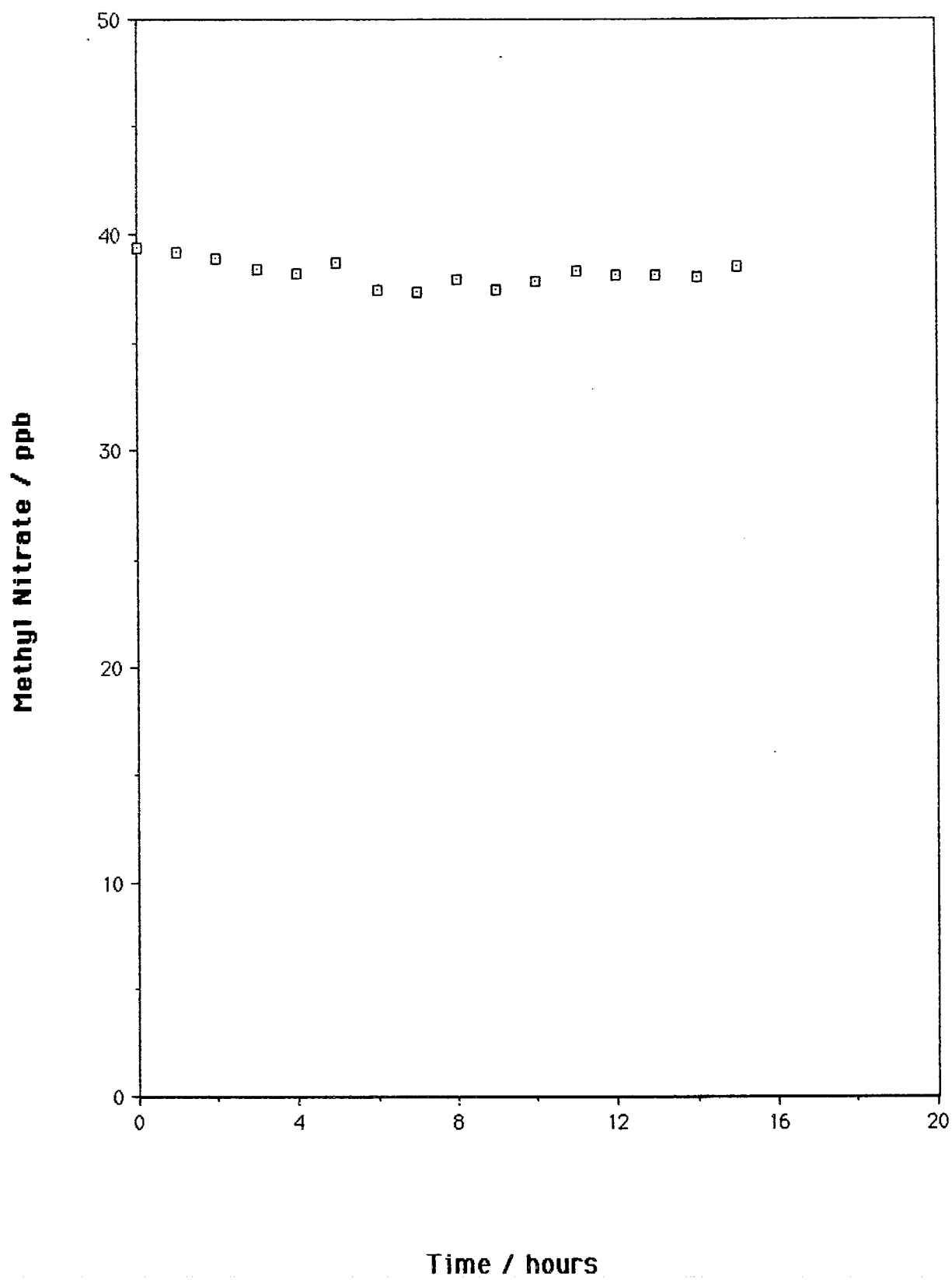


Figure 6. MethylNitrate Calibration with Electron Capture and Chemiluminescence Detectors

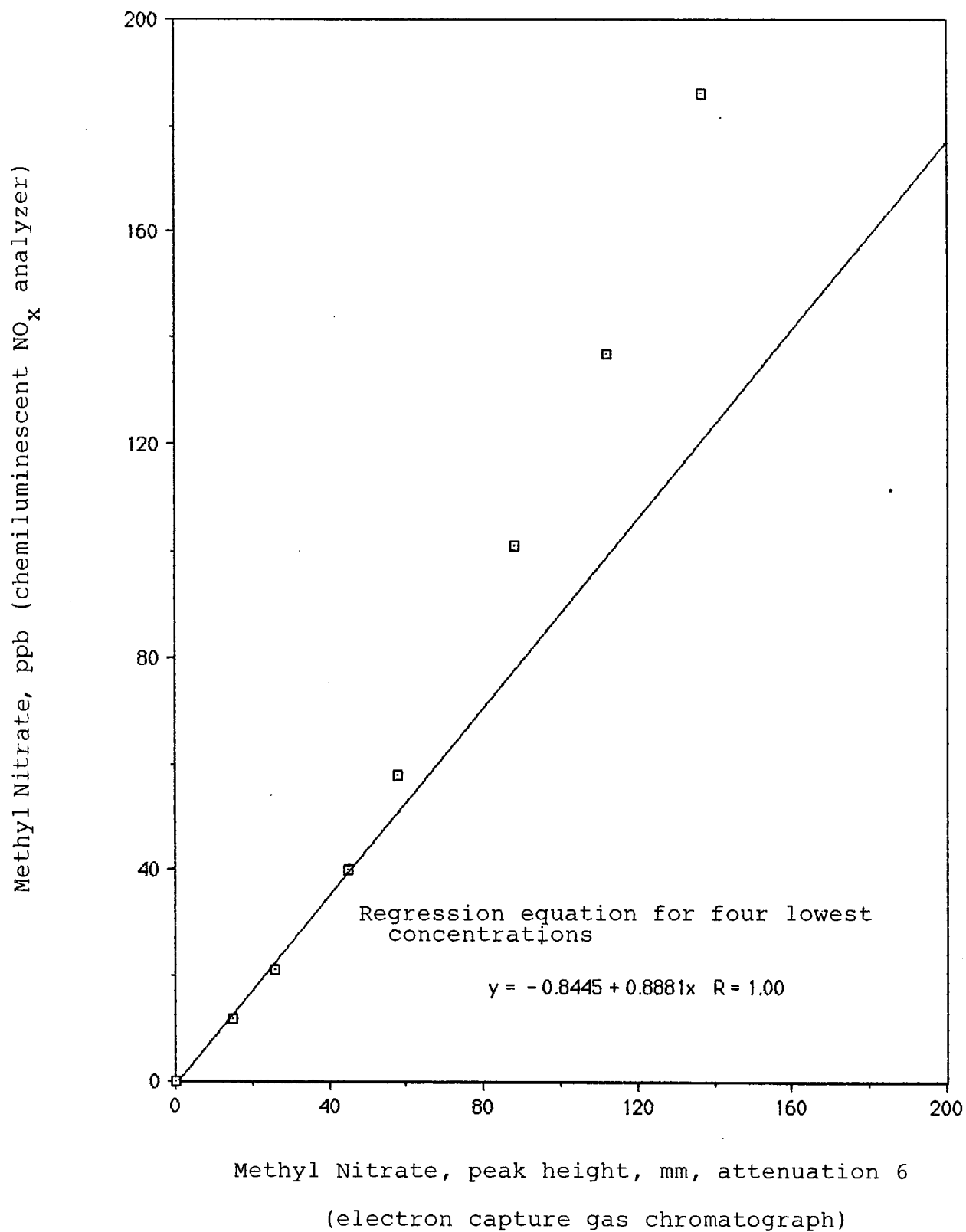
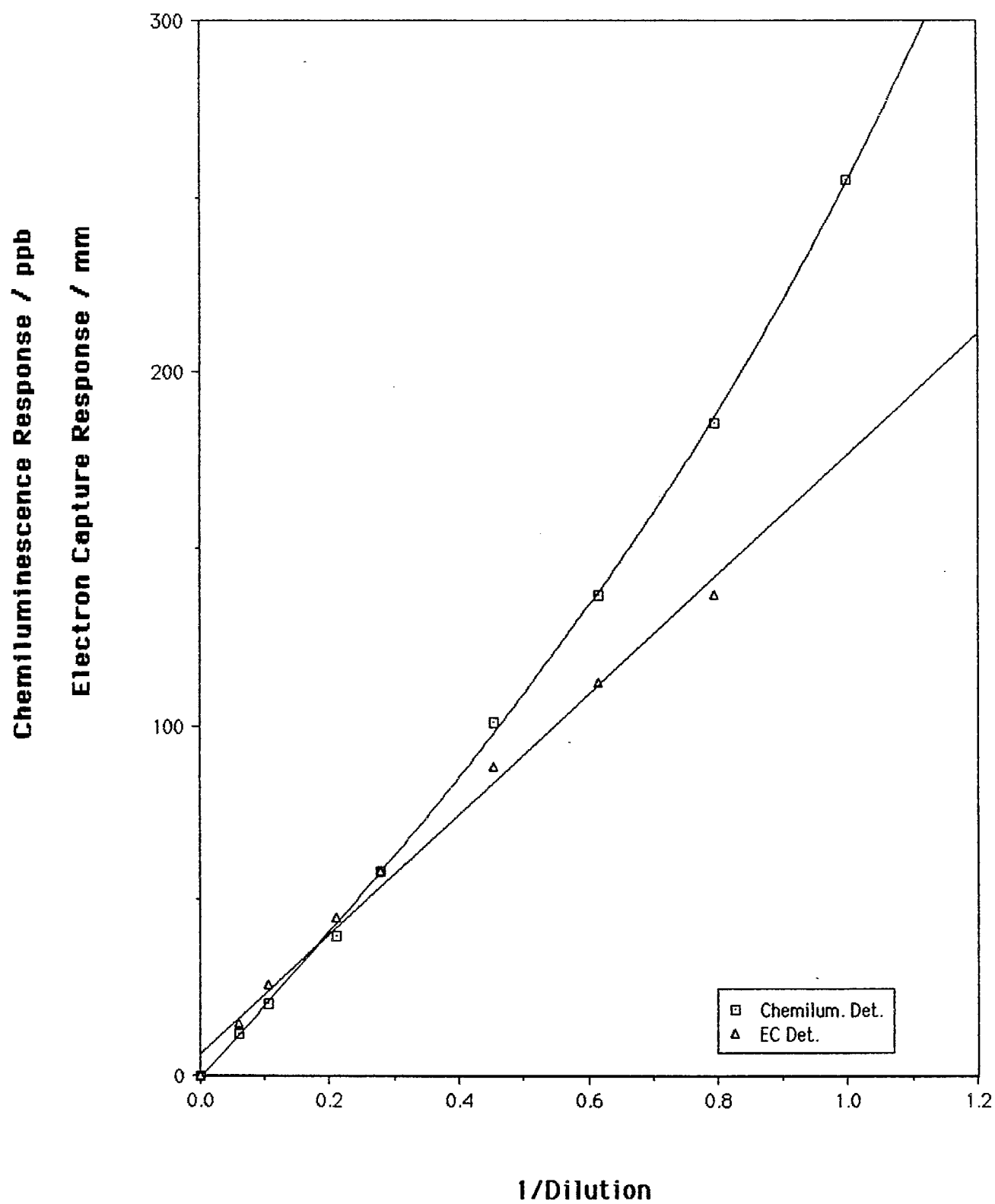


Figure 7. Methyl Nitrate Calibration: ECD and Chemiluminescence Detectors Response as a Function of Dilution



## 5. INTERLABORATORY COMPARISON STUDIES

Several groups besides DGA carried out PAN measurements during SCAQS. The U. of Denver group (Claremont, June 87 only) and Unisearch (Long Beach, fall only) employed different versions of the luminol method. The U.S. EPA group (Claremont, summer only) and the GM group (captive air measurements only, ambient PAN not measured) employed the method also used by DGA, i.e. electron capture gas chromatography (EC-GC).

Different EC-GC calibration methods were employed, namely infrared spectroscopy (EPA), liquid chromatography-uv detection measurement of acetate following alkaline hydrolysis of PAN (DGA), and chemiluminescence (DGA). The GM group also performed frequent instrument stability checks using known amounts of carbon tetrachloride.

In the absence of any formal QA regarding PAN measurements during the summer phase of SCAQS, informal comparisons initiated by the participants were carried out. Results of these field comparisons, which were not supported by the ARB, are included in this report because of their obvious relevance to this project. The ARB subsequently sponsored DGA to participate in a laboratory comparison held at the U.S. EPA laboratory. As this study was more comprehensive in scope and included a direct comparison of calibration methods, it is described first, followed by summaries of the field comparisons.

A memorandum summarizing preliminary results of the summer 1987 intercomparison studies was issued by DGA on October 22, 1987 and distributed to U.S. EPA, U. of Denver, GM and ARB staff. Since this memo was issued, our PAN concentrations for the periods of interest have been revised downwards by 3.7% in Azusa (comparison with U. of Denver) and in Claremont (comparison with EPA). These small changes do not affect the overall conclusions that can be drawn from the field comparison studies.

### 5.1 Laboratory comparison: EPA and DGA

#### 5.1.1 Study scope

The laboratory comparison was carried out on September 7-9, 1988, at the U.S. EPA Atmospheric Sciences Research Laboratory (ASRL), Research Triangle Park, N.C. The comparison involved the following components:

- Preparation, by NSI Technology Services Corporation, of 2 Tedlar bags containing 13.0 and 42.0 ppm of PAN, respectively, as measured by EPA using infrared spectroscopy. PAN was synthesized at NSI in tridecane according to an adaptation of published methods (Nielsen et al 1982, Gaffney et al 1984).
- Dilution, using pure air and a calibrated mass flow controller, of the contents of the 2 Tedlar bags to yield eight concentrations of PAN in Teflon bags. These were also prepared by NSI.
- Side-by-side EC-GC measurements, by DGA and EPA, of PAN concentrations in the eight diluted samples.
- Comparison of the DGA and EPA calibration methods, i.e. infrared spectroscopy (EPA), NO<sub>x</sub> chemiluminescence (EPA) and PAN alkaline hydrolysis to acetate (DGA). NO<sub>x</sub> measurements of the diluted PAN samples were also carried out at NSI.
- Comparison of two samples of methyl nitrate, one synthesized at DGA and the other at EPA.

### 5.1.2 Experimental methods

DGA employed the EC-GC instrument they had operated in Claremont during SCAQS. The EC-GC employed by EPA during SCAQS was not available for this study; another similar (but older) instrument was used. The DGA instrument (Valco 140BN detector, 5 mC <sup>63</sup>Ni foil, 3 ft x 1/8 inch FEP Teflon column, 10% Carbowax 400 on 60/80 mesh acid washed, DMCS-treated Chromosorb P) was operated with nitrogen carrier gas; the column and detector temperatures were 36°C and 60°C, respectively. The EPA instrument (Analog Technology Corp. 140B, 10 mC tritiated scandium detector, 2 ft x 1/8 inch nickel column, 10% Carbowax 1000 on 60/80 mesh Gas Chrom Z) was operated with argon-methane carrier gas; both column and detector were at ambient temperature.

The EPA calibration procedure involved infrared spectroscopy analysis (Shimadzu IR-460 with 7.2 m path cell) of 10-12 ppm PAN samples prepared by dilution of pure PAN in air in Tedlar bags. These samples are then further diluted in pure air to yield 0-50 ppb PAN (in 2 mil Teflon FEP bags) for EC-GC analysis. The DGA calibration procedure involves NO<sub>x</sub> chemiluminescence and PAN alkaline hydrolysis to acetate, see Section 4.1 for details. Two NO<sub>x</sub> analyzers were available during the study, one at NSI (Monitor Labs 8840) and one at EPA ("high flow" version of ML 8840, flow rate = 2 lpm). Both were calibrated by gas

phase dilution of certified NO in nitrogen calibration gases (e.g. 53 ppm NO diluted with Teco 101 calibrator at EPA). For cross-comparison, the output of the certified NO<sub>2</sub> permeation tube used by DGA to calibrate their NO<sub>x</sub> analyzer (which was not brought to EPA for this study) was measured using the EPA NO<sub>x</sub> instrument.

### 5.1.3 Correction for PAN loss

DGA calibrations are normally carried out using a stable source of PAN (e.g.  $\pm 2\%$  over 12 hours). Unfortunately, PAN concentrations in the samples prepared at NSI were not stable over the time scale of the comparison study, see Table 8. Since EC-GC, NO<sub>x</sub> and alkaline cartridge measurements were of necessity carried out at different times, the PAN decay must be taken into account. A log plot of concentration vs. time for all but one bag sample yielded a first-order decay behavior, see Figure 8. Regression analysis of the data in Figure 8 yielded a slope of  $(1.57 \pm 0.3) \times 10^{-3}$  and a near-zero intercept,  $(1.18 \pm 1.88) \times 10^{-3}$ , with  $R = 0.84$ . Decay-corrected PAN peak heights and peak areas were calculated using these parameters and are listed in Table 9.

One bag sample yielded different PAN loss results, see Figure 9. The initial PAN loss rate was lower than for other bags (this bag had a lower initial surface to volume ratio). The PAN loss rate subsequently increased as the bag volume was depleted by collection of two alkaline cartridge samples. Loss-corrected PAN concentrations for this bag samples were estimated from Figure 9 at the median times of cartridge collection, 109 and 211 minutes.

### 5.1.4 Comparison of calibration methods

Data for alkaline cartridge samples analyzed for their acetate content upon return to DGA are compared in Table 10 to those obtained at the time of the study by IR and by NO<sub>x</sub> chemiluminescence. Good agreement is observed between the acetate and IR methods. Reasonable agreement was also obtained between acetate and NO<sub>x</sub> methods. Acetate data at low PAN concentrations are lower than the corresponding NO<sub>x</sub> measurements, as should be the case since PAN was lost between the NO<sub>x</sub> measurements and the acetate measurements which were carried out up to several hours later.

TABLE 8. OBSERVED PAN DECAY DURING EPA-DGA  
LABORATORY COMPARISON STUDY

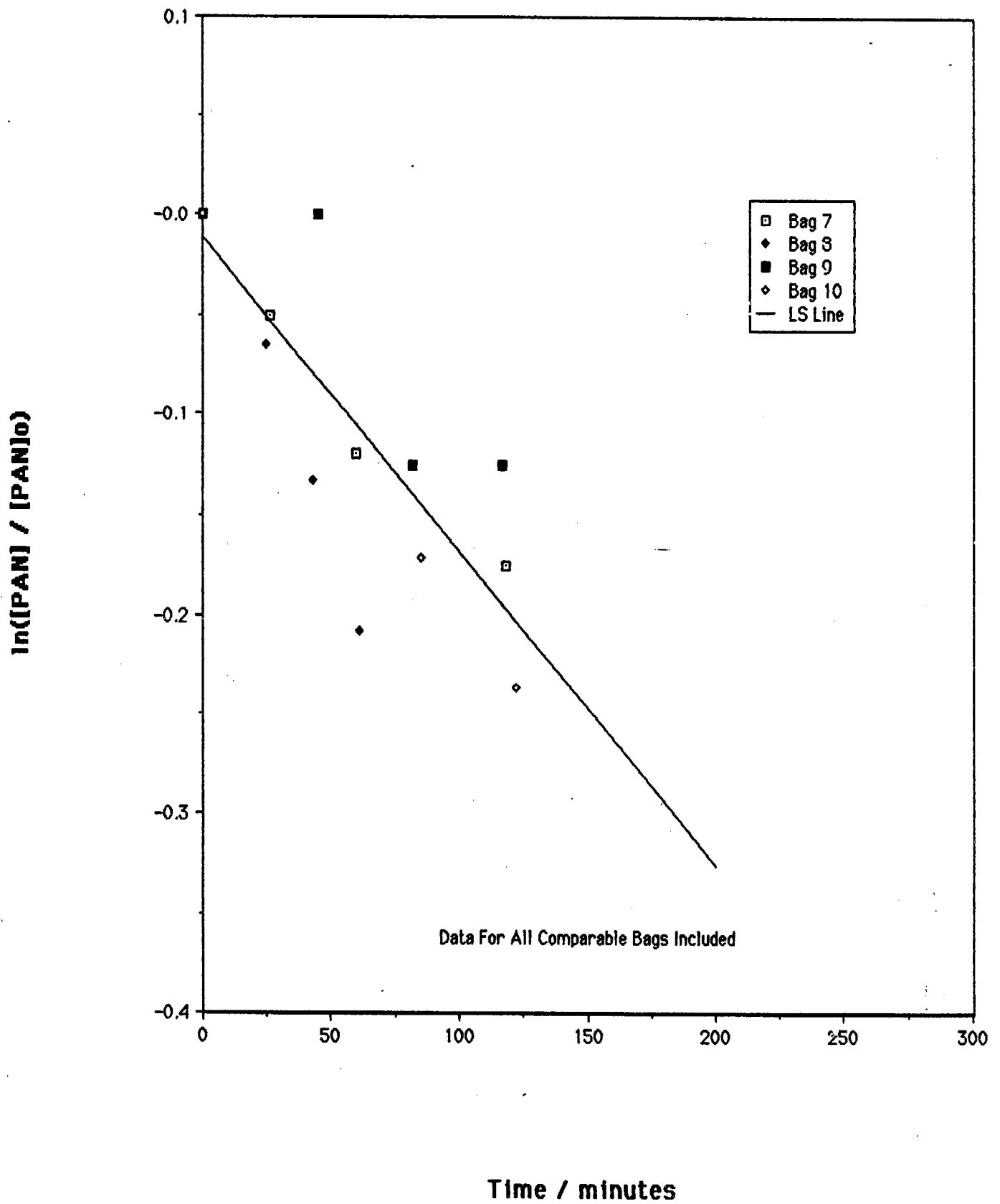
DGA EC-GC Measurements				EPA and NSI NOx Measurements			
Bag	Time, EDT	Peak Height mm(a)	Att	Bag	(NOx - NO) ppbv Time	EPA	NSI
15	12:47	60	3	7	12:29		195
15	13:38	47	3	7	13:57	178	
14	10:58	27	7	8	14:33		75
14	11:40	26.5	7	8	12:33	73	
14	13:54	24.5	7	9	15:34	13	
14	14:59	22	7	9	16:45		10
16	14:36	6	3	10	17:23		25
16	15:49	7	3	10	17:39	25.5	
4	17:04	56	5	6L	10:09(b)	49.7	
4	18:04	47	5				
4	18:29	44	5				
4	18:54	43	5				
7	11:47	62	6				
7	12:13	59	6				
7	12:47	55	6				
7	13:45	52	6				
8	14:07	32	6				
8	14:32	30	6				
8	14:50	28	6				
8	15:08	26	6				
9	15:43	17	4				
9	16:28	17	4				
9	17:05	15	4				
9	17:40	15	4				
10	17:58	19 ± 2	5				
10	18:37	16	5				
10	19:14	15	5				
11	8:46	0	3				
6L	9:27	34	5				
6L	10:16	33	5				
5	18:16	33 ± 0.5	10				

(a) uncertainty of ± 1 mm unless otherwise indicated.

(b) 9/9/88; all other data 9/8/88.



FIGURE 8. FIRST ORDER PAN LOSS RATE  
(ALL SAMPLES EXCEPT BAG 14)



**TABLE 9. DGA PAN PEAK HEIGHTS AND PEAK AREAS  
CORRECTED FOR PAN DECAY IN TEFLON AND TEDLAR BAGS**

	Measured (a)		Corrected (b)		Elapsed time, min. (c)	NOx		Acetate
	Peak Area $10^{-6}$ counts	Peak Height mm, (att 3)	Peak Area	Peak Height		NSI ppb	EPA ppb	DGA ppb
7	1.57	496	1.47	464	42	195		
7	1.57	496	1.28	405	126		178	
8	0.79	256	0.758	246	26	75		
8	0.79	256	0.745	241	37		73	
9	0.0934	34	0.0954	34.7	-13		13	
9	0.0934	34	0.0846	30.8	62	10		
10	0.184	76	0.207	74.7	11	25		
10	0.184	76	0.202	72.8	27		25.5	
11	0	0					1.0± 1	
14	1.36	424	1.315	408(d)	67			154± 4
14	1.27	392	1.165	372(d)	32.5			137± 3
6L	0.381	136	0.381	136	(e)		49.7	

(a) Peak area and height from the first injection of the bag contents.

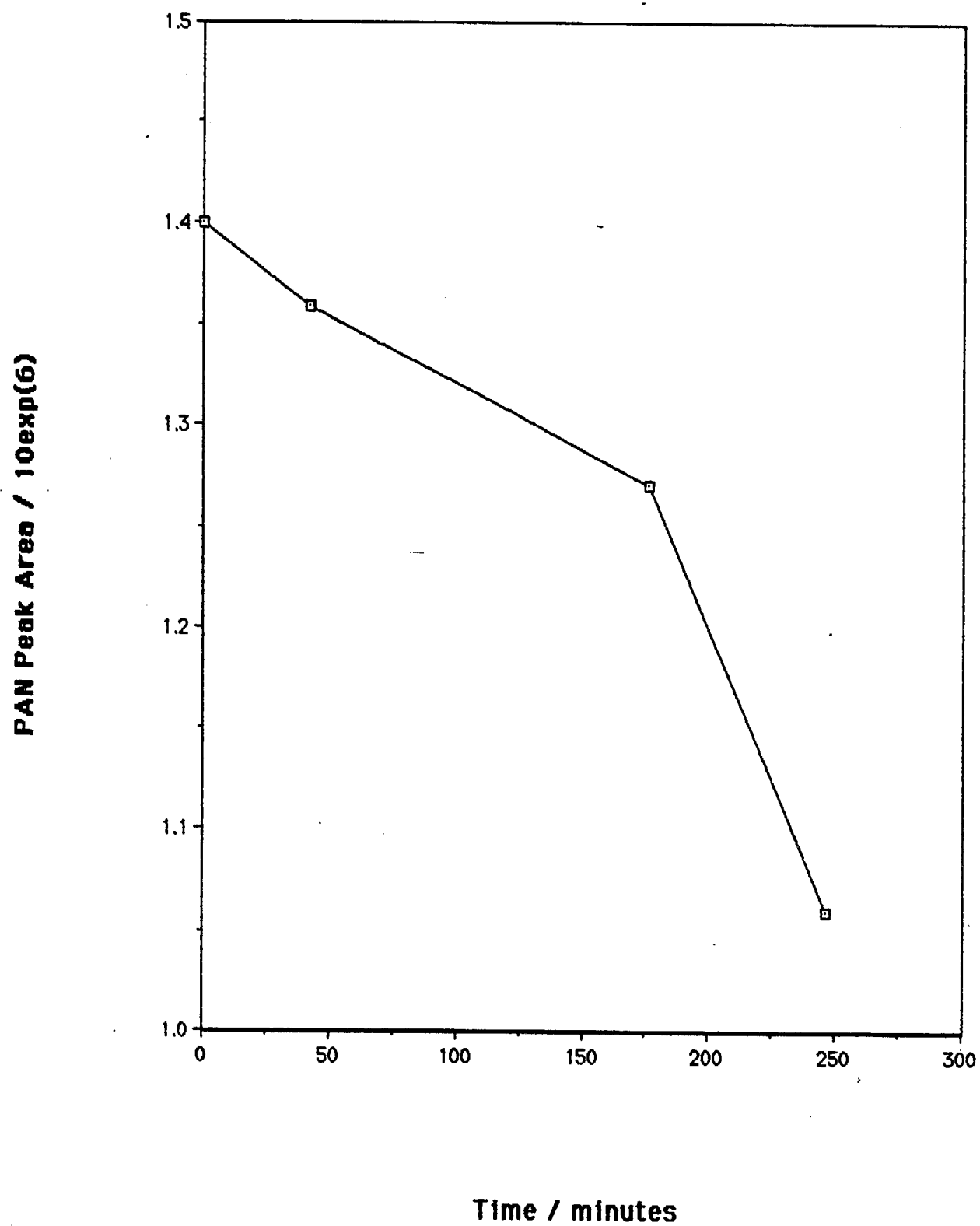
(b) Peak area and height were corrected using the equation:  $[PAN] = [PAN]_0 \exp \{ -[(1.57 \times 10^{-3}) * T + 1.18 \times 10^{-3}] \}$  where T is the time interval between the first injection on the GC and the NOx or acetate measurement, [PAN] and [PAN]<sub>0</sub> are the calculated (columns 4 and 5) and the initial (columns 2 and 3) peak area or height, respectively. This equation was obtained from a regression fit to the data in Figure 8.

(c) Time interval, T, from the first injection on the GC to NOx measurements (columns 7 and 8) or acetate measurements (Column 9).

(d) Calculated from Figure 9, see text.

(e) No [PAN] decay was observed.

FIGURE 9. PAN LOSS RATE FOR BAG 14



**TABLE 10. COMPARISON OF ALKALINE HYDROLYSIS  
AND OTHER CALIBRATION METHODS**

Bag Number	Cartridge Number	Collection Time, min.	Flow rate, lit. /min	Acetate, $\mu\text{g}$	PAN concentration, ppm		NSI
					DGA-Acetate	EPA-IR	
	1	5	$0.95 \pm 0.02$	$166 \pm 20$	$14.5 \pm 1.7$	13.0	
14	2	121	$0.87 \pm 0.02$	$39.0 \pm 0.1$	$0.154 \pm 0.004$		0.19
14	3	60	$0.88 \pm 0.02$	$17.6 \pm 0.1$	$0.138 \pm 0.0003$		0.19
14	4	0.08	$0.88 \pm 0.02$	0	0		0.19
	5(a)	22	$0.87 \pm 0.02$	$161 \pm 27$	$3.5 \pm 0.6$		2.97

(a) unknown PAN sample

### 5.1.5 Calibration factors for DGA instrument

From the data in Table 9, calibration factors were calculated for the DGA PAN analyzer. The peak area vs. PAN concentration plot is shown in Figure 10. The slope of the corresponding regression line ( $R = 0.99$ ) yields a calibration factor of  $0.388 \pm 0.001$  ppb/mm. The corresponding peak area calibration factor is  $123$  ppb/ $10^6$  counts.

It is of interest to compare these calibration factors to those obtained at DGA with the same instrument. The peak area calibration factors (units: ppb/ $10^6$  counts) were  $75.0 \pm 4.1$  in October 1987 (SCAQs calibrations),  $72.8 \pm 4.8$  in January-February 1988 (post-SCAQs calibration),  $105.3 \pm 0.15$  in July 1988 (DGA study of indoor-outdoor levels of PAN in Southern California), and  $96.2 \pm 0.13$  in November 1988 (DGA smog chamber studies). Not unexpectedly, the comparison suggests a possible decrease in detector sensitivity with time for this heavily used instrument.

### 5.1.6 Comparison of PAN results

The results of the comparison are summarized in Table 11. For all eight samples, values reported by DGA are within  $13 \pm 4\%$  of those "prepared" by NSI (approximate levels of PAN were known for five samples; the other three were unknown and were made available by NSI to DGA and EPA after all data were reported). The corresponding regression equation is:  $\text{PAN (DGA)} = 0.87 \pm 0.04 \text{ PAN (NSI)} + (3.9 \pm 4.6)$ ,  $n = 8$ ,  $R = 0.993$ , units: ppb. EPA and DGA agreed within 10% on two of the five samples (bags 9 and 10) for which data were reported by both groups. The high concentration sample, bag 8, was beyond the range of PAN usually covered by EPA in their calibration. For the remaining two samples, (bags 15 and 16) the two groups are off by a factor of two, or some 33% of the average of their reported values.

A number of difficulties were encountered with the EPA instrument during the study, including low standing current and non-linear response to PAN at concentrations higher than 30 ppb. These difficulties are not relevant to EPA's measurements during SCAQS, which were performed with another instrument. A comparison of EPA and DGA SCAQS data is presented in Section 5.2.

### 5.1.7 Methyl nitrate comparison

IR spectra were recorded at EPA of samples of methyl nitrate synthesized at EPA and DGA, respectively. The spectra are shown in Figure 11 and are essentially identical.

FIGURE 10. DGA PAN ANALYZER CALIBRATION DURING  
EPA-DGA COMPARISON STUDY

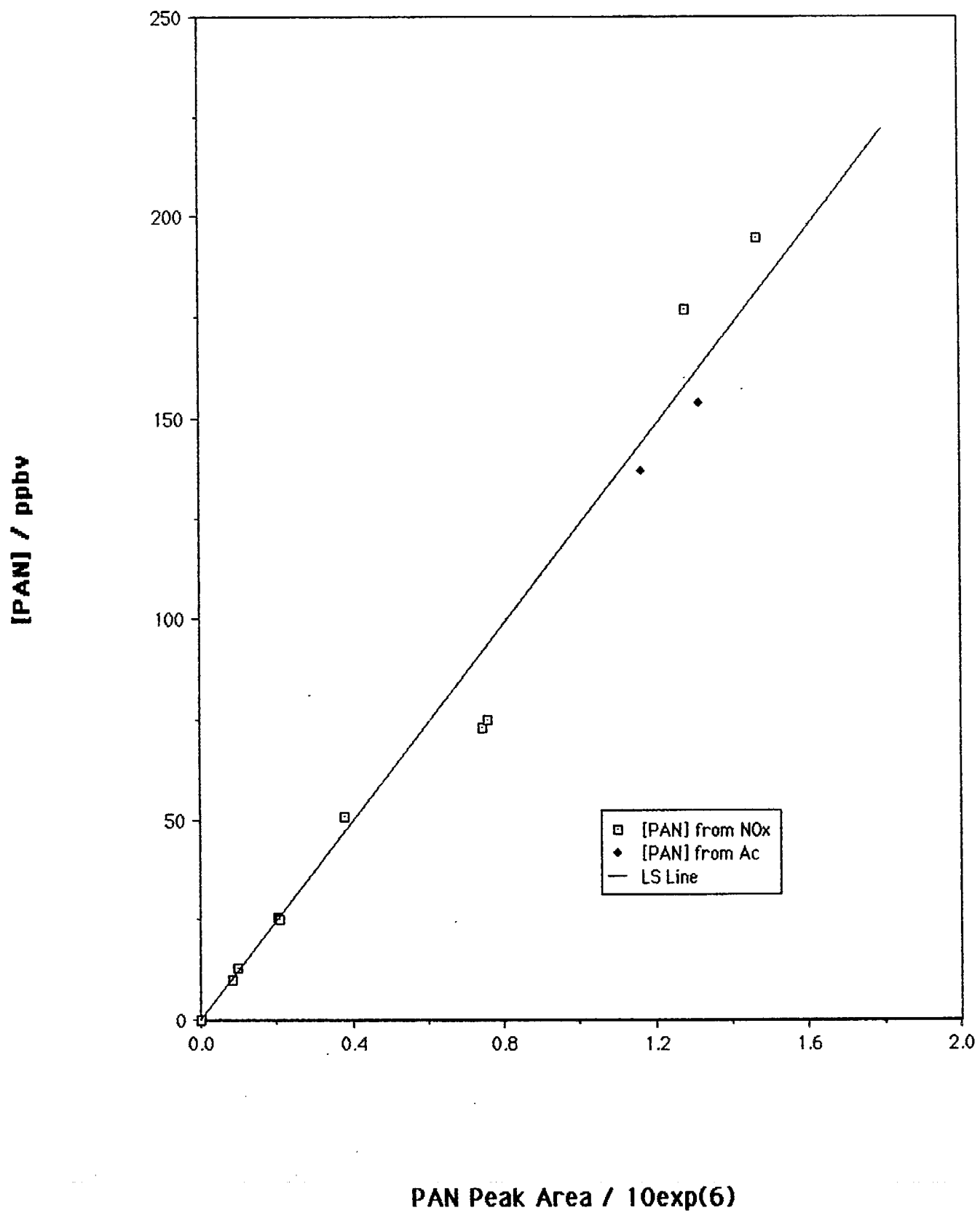


TABLE 11. COMPARISON OF PAN RESULTS

Bag	Time EDT	DGA [PAN](a)		Time EDT	EPA [PAN](b)		NSI Dilution ppb	[PAN] Ratios(c)		
		Peak Area ppb	Peak Height mm		Peak Area ppb	Peak Height mm		DGA/EPA	DGA/NSI	EPA/NSI
7	11:47	194	192		ND	ND	227	ND	0.85	ND
8	14:07	97.5	99.3	14:19	ND	ND	81.6	ND	1.20	ND
9	15:43	11.5	13.1	15:08	9.7	9.1	10.2	1.19	1.13	0.95
10	18:37	23	25	17:49	25.2	26.4	26.3	0.91	0.87	0.96
14	10:58	172	168				190	ND	0.91	ND
15(d)	13:38	17	18	13:59	25.4	27.4	17.4	0.67	0.98	1.46
16(d)	15:49	2.2	2.7	15:04	4.3	4.4	2.44	0.51	0.90	1.76
16(d)	14:36	2.3	ND				2.44	ND	0.94	ND

(a) DGA calibration factors:  $123.4 \times 10 \exp(-6)$  ppb/(area count) and 0.3879 ppb/mm

(b) EPA calibration factors of  $3.0 \times 10 \exp(-6)$  ppb/(area count) and 0.114 ppb/mm used with average peak areas and peak heights.

(c) PAN concentration ratios calculated from EPA and DGA reported peak area PAN concentrations.

(d) Unknown PAN samples.

FIGURE 11a. INFRARED SPECTRUM OF METHYL NITRATE. DGA SAMPLE.

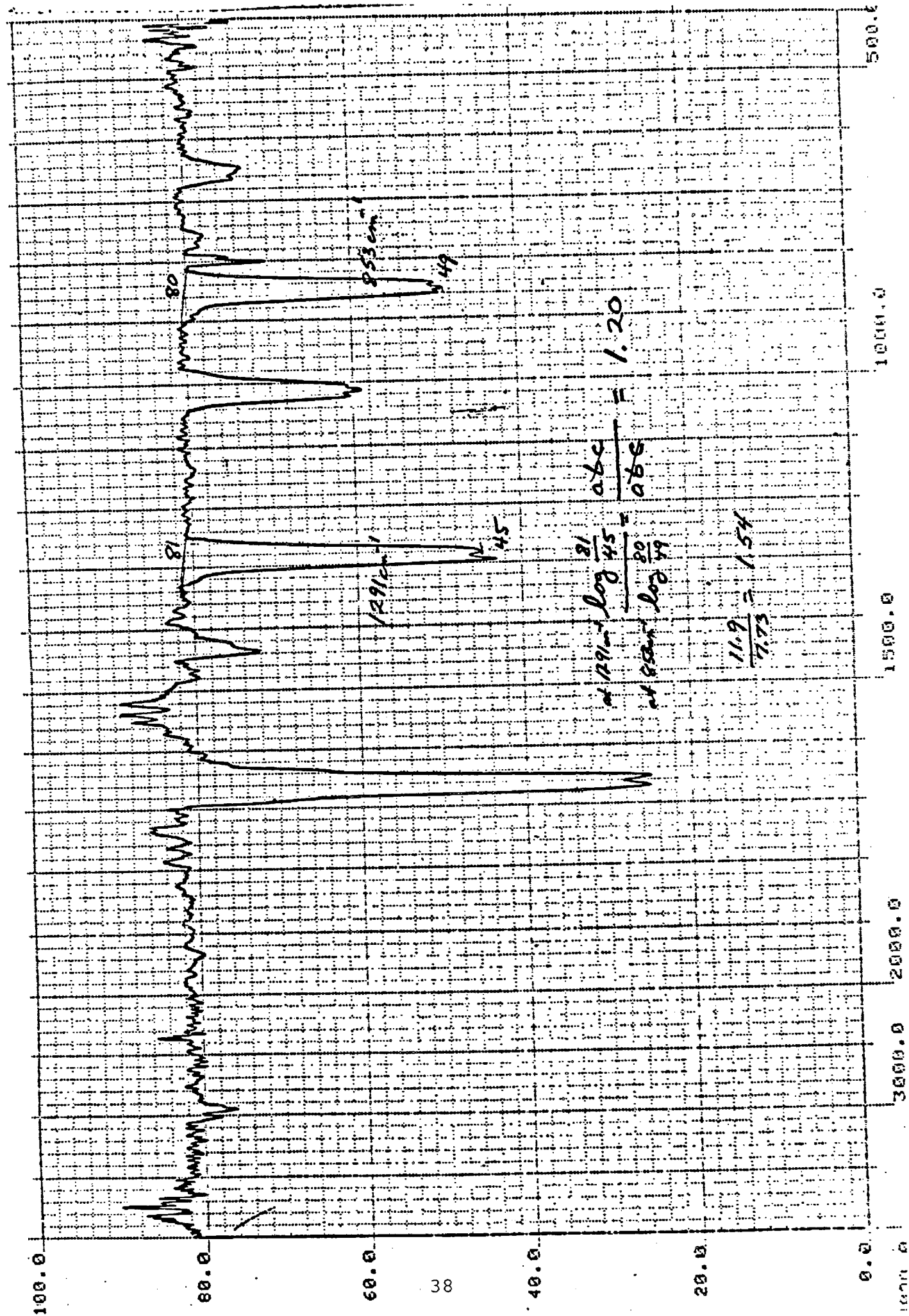
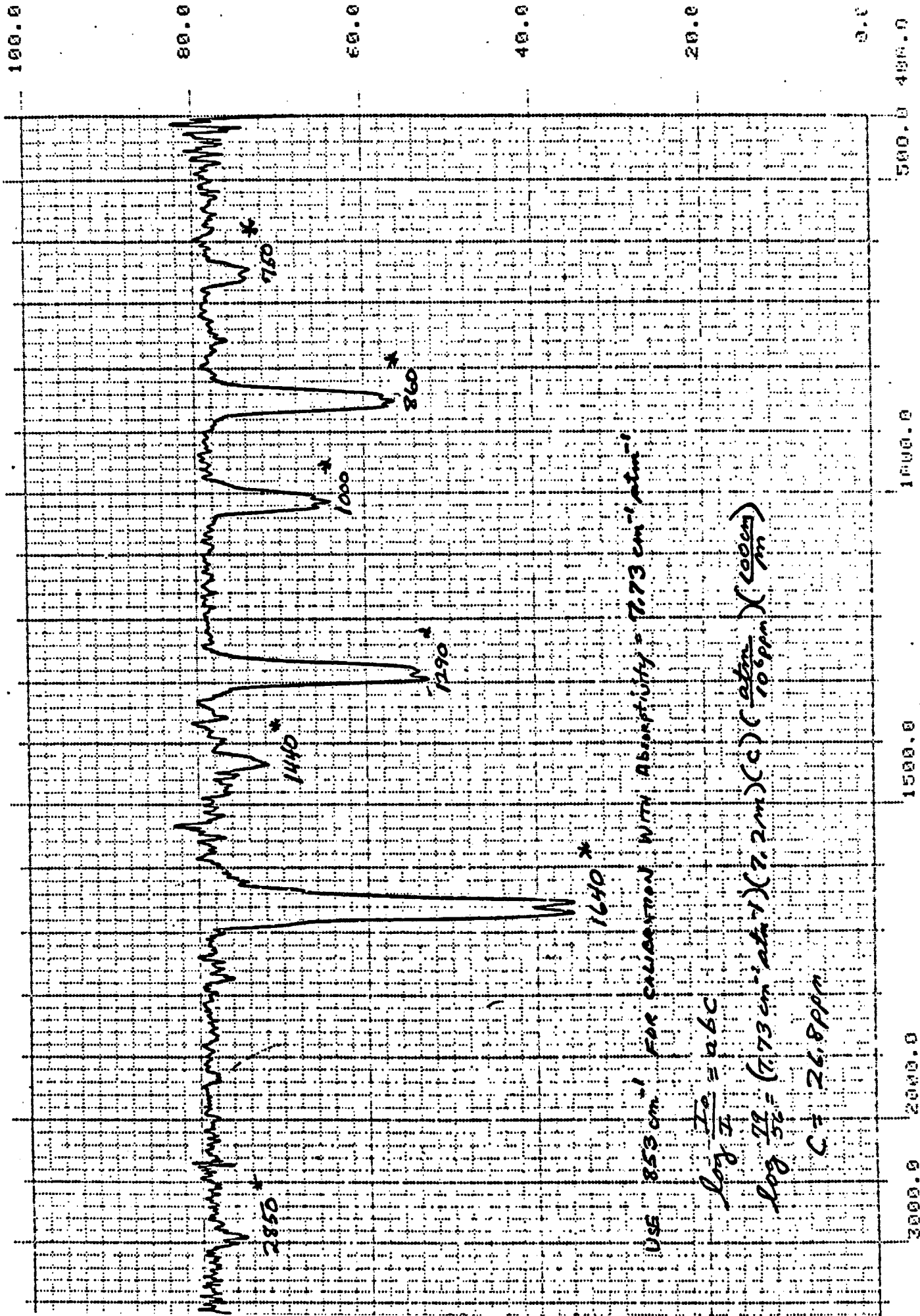




FIGURE 11b. INFRARED SPECTRUM OF METHYL NITRATE. EPA SAMPLE.



Both groups employ different calibration methods:  $\text{NO}_x$  chemiluminescence (DGA, see Section 4.2 for details) and infrared spectroscopy (EPA). Three samples of methyl nitrate in pure air were prepared, and their concentration measured by IR prior to dilution. The results are summarized in Table 12. Departure from linear response is observed at the highest concentration tested, 30.8 ppb (assuming there was no error in the IR measurement and/or the subsequent dilution). Good agreement was observed for the two samples with lower methyl nitrate concentrations, 7.2 and 10.3 ppb. The DGA response factor calculated from the data in Table 12, 0.106 ppb/mm, is within 12% of that (0.121 ppb/mm) determined at DGA in June 1988 using a different calibration method,  $\text{NO}_x$  chemiluminescence. There is presently some uncertainty (~20%) as to the appropriate IR data to be used for calibration, see footnote in Table 12.

## **5.2 Field comparison: EPA and DGA**

This comparison included two components, one involving EPA readings of the output of the DGA PAN generator (9/5/87) and the other involving comparison of ambient PAN in Claremont (8/27-29/87) where both groups operated similar EC-GC instruments. No side-by-side comparison was carried out: the DGA instrument was first operated in the ARB trailer and subsequently at nearby Seaver Hall (some 200 ft and 0.5 mile, respectively, from the EPA mobile laboratory).

Some fifty readings of the DGA PAN generator output were taken by EPA at seven dilutions corresponding to 10-300 ppb of PAN (Figure 12). The PAN generator was then moved to Seaver Hall where an attempt was made to obtain PAN outputs identical to that produced in the EPA mobile lab, thus allowing for an indirect comparison of the two EC-GC instruments.

Assuming that the same PAN outputs were obtained, and using the appropriate calibration factor for the DGA instrument operated at Seaver Hall, we initially reported (10/87 memorandum cited earlier) that the data were best fit by  $\text{PAN (DGA)} = 0.64 \text{ PAN (EPA)} - 3.8$ ,  $R = 0.978$ ,  $n = 7$ . Our initial assumption was incorrect, i.e. only similar (within 30-40%), but not identical, stable PAN outputs could be obtained when moving the generator from location to location during SCAQS. Thus the results of this component of the study are simply taken to mean that (a) PAN production in the generator was independently confirmed by a second

TABLE 12. COMPARISON OF METHYL NITRATE RESULTS

Nominal concentration, ppb(a)	Bag number	DGA		EPA	
		Peak height, mm(b)	Peak area /10 <sup>6</sup> counts	Peak height, mm(c)	Peak area /10 <sup>6</sup> counts
10.3	19	94	0.0933	36.5	0.344
		93	0.0915	35.2	0.323
		96	0.0931	35.5	0.335
7.25	20	70	0.06	55.0	0.262
		70	0.0646	55.3	0.267
		ND	ND	56.0	0.263
30.8	21	380	0.382	59.2	2.25
		364	0.364	59.8	2.248
		ND	ND	60.8	2.308

Calibration factors calculated from above (d)

Group	Peak Area Response ppb/count	Peak Height Response ppb/mm
EPA	$(2.91 \pm 0.24) \times 10^{-5}$	$0.0345 \pm 0.0021$
DGA	$(1.14 \pm 0.04) \times 10^{-4}$	$0.106 \pm 0.002$

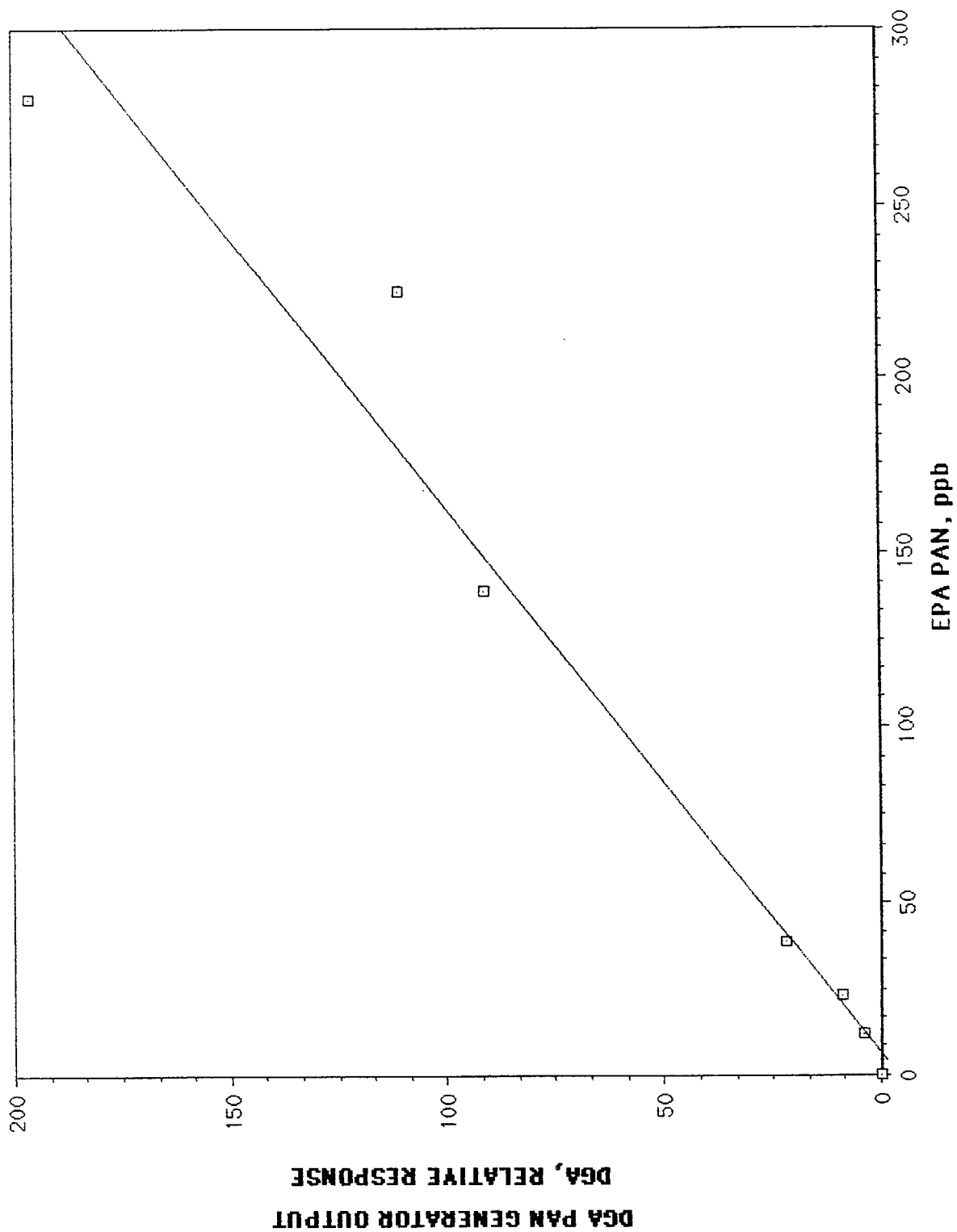
(a) as measured by IR before dilution. Absorptivity coefficients (units:  $\text{cm}^{-1}\text{atm}^{-1}$ ) used for methyl nitrate calibration are 7.73 at  $853\text{ cm}^{-1}$  at EPA (used in this work) and 11.9 at  $1291\text{ cm}^{-1}$  at U.C. Riverside (E. Tuazon to B. Gay, 9/88). The ratio is 1.54 vs. only 1.2 in Figure 11.

(b) attenuation 3

(c) attenuation 8

(d) excluding bag 21 data.

FIGURE 12. EPA MEASUREMENTS OF OUTPUT OF DGA PAN GENERATOR,  
CLAREMONT, CA, 9/87



laboratory (b) the EPA instrument responded linearly to dilutions of the PAN generator output, and (c) indirect comparison suggests that the two instruments were within some 30-40% of each other, with most of the difference being due to changes in generator output.

Ambient data obtained in Claremont by the two groups are compared in Figures 13 and 14, which were prepared by E. Fujita (ARB). The time series plot in Figure 13 shows good tracking of PAN diurnal variations for the three GO days August 27-29, 1987. The overall data set was best fit by the equation  $PAN(EPA) = 0.775 PAN(DGA) - 0.6$ ,  $R = 0.99$ ,  $n = 66$ , units: ppb (Figure 14). Since both groups have made all of their Claremont data available to the ARB, the comparison described above could be extended to the entire data set.

### 5.3 Field comparison: Unisearch and DGA

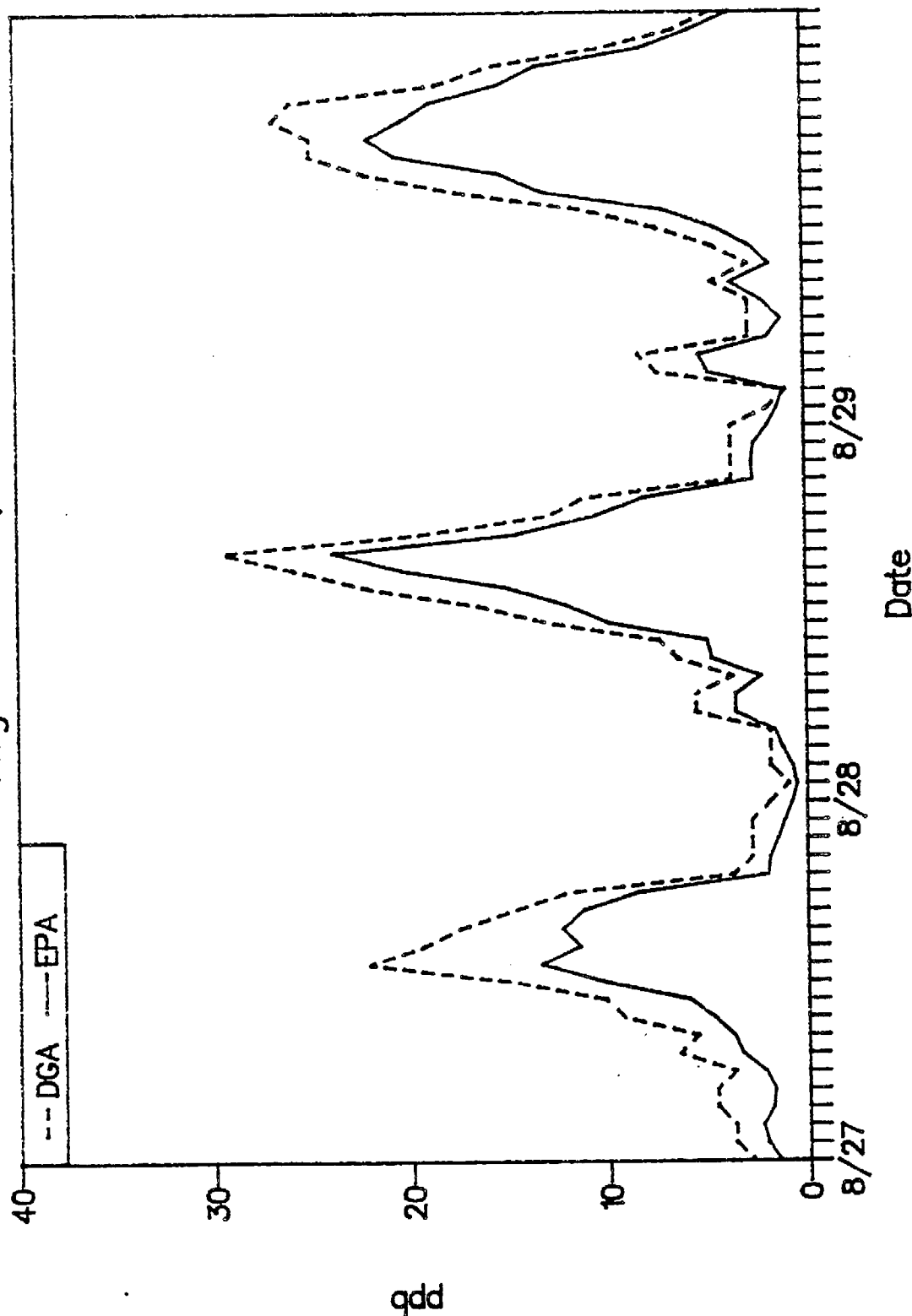
This study was carried out on December 14, 1987 at the Long Beach SCAQS site, where DGA and Unisearch took side-by-side readings of the undiluted (DGA only) and diluted (both groups) output of the DGA PAN generator. Both groups measured PAN with the instrument they had operated to measure ambient PAN in Long Beach during the winter phase of SCAQS, i.e. a prototype luminol instrument (Unisearch) and an electron capture gas chromatograph (DGA). Dilution flow rates were set using a calibrated mass flow controller and were selected by a "third party," Eric Fujita (ARB) with assistance from Kochy Fung (ERT). The full output of the DGA PAN generator operated at a flow rate of 142 mL/min. was 365 ppb. The output was diluted with pure air (dilution air flow rate of up to 10L/min.) to yield nominal PAN concentrations of about 5, 10 and 25 ppb.

Table 13 summarizes all DGA data along with data made available to us by other study participants. The Unisearch PAN concentrations reported in Table 13 are those reported to E. Fujita (ARB) on October 26, 1988. These concentrations are substantially different from those quoted by Dr. G. MacKay (who operated the Unisearch instrument) on the day the comparison took place. Figure 15 shows that the DGA instrument responded linearly to all dilutions of the PAN generator output. Figure 16 compares DGA and Unisearch PAN concentrations and gives the corresponding regression parameters.

Figure 13. Time Series Plot of Ambient PAN Data (Source:  
E. Fujita, ARB Research Division)

# Peroxyacetyl Nitrate, DGA vs EPA

SCAQs, Claremont  
August 27-29, 1987



ARB-RO, 1989

FIGURE 14. SCATTER PLOT OF DGA AND EPA AMBIENT PAN DATA

(SOURCE: E. FUJITA, ARB RESEARCH DIVISION)

## Peroxyacetyl Nitrate, DGA vs EPA

Claremont, August 27-29, 1987

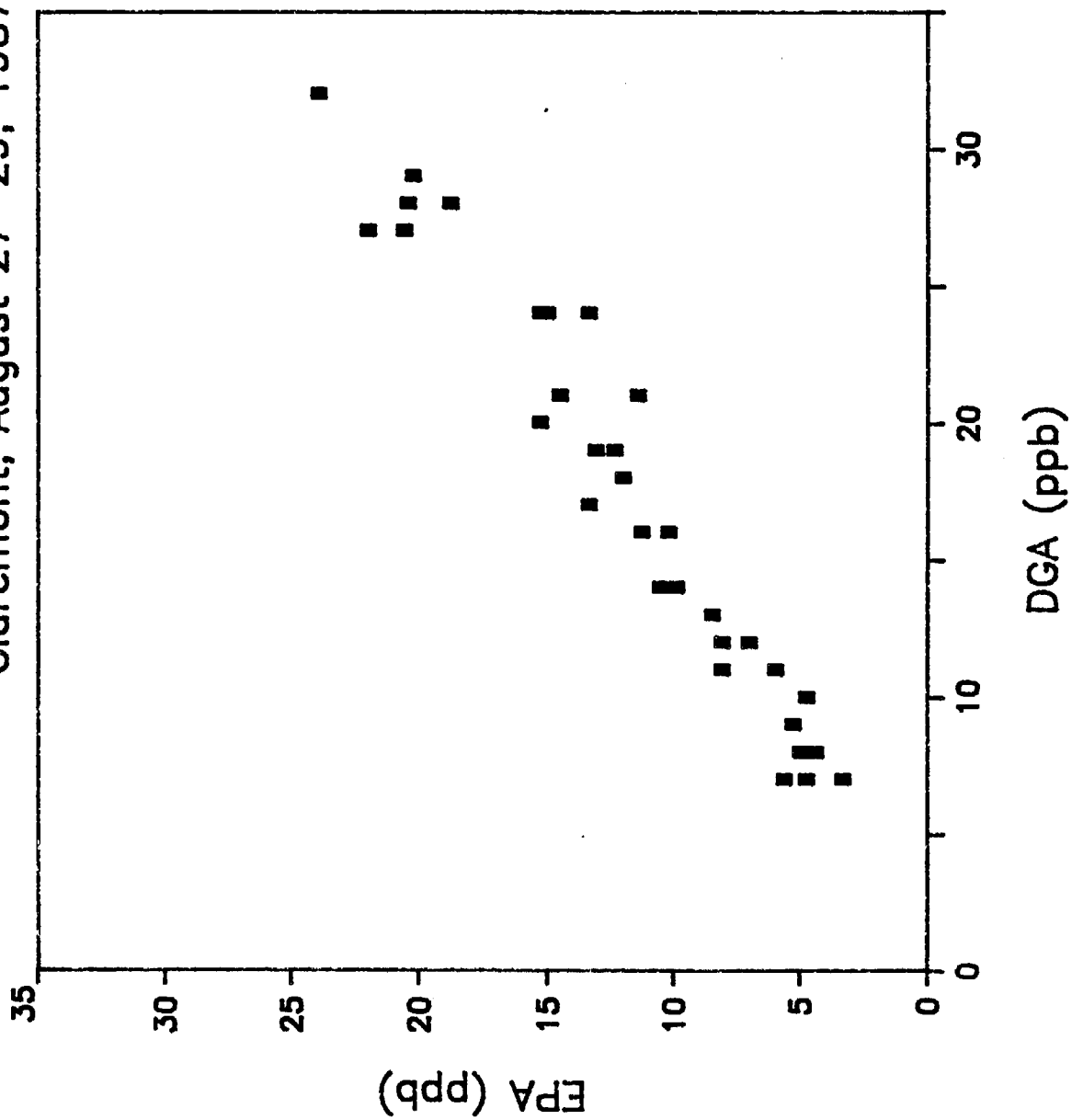


TABLE 13. RESULTS OF THE UNISEARCH-DGA COMPARISON STUDY											
LONG BEACH PAN COMPARISON STUDY											
TIME	PAN	PAN	PAN	Reactor	Dilution	Dilution	PAN from	DGA	Unisearch		
	Retention	Peak Height	Peak Area	Flow	Flow	Factor	Dilution	PAN	PAN		
/PST	Time	Att-3	/10 exp(6)	Fr	Fd	1/(Fr+Fd)	/ppb	/ppb	/ppb		
	/min.	/mm		ml/min.	ml/min.	/10 exp(4)					
10:44	8.18	592	3.42	142	0	70.42	337	325			
11:13	8.75	632	3.75	142	0	70.42	337	347			
11:38	9.04	616	4.05	142	0	70.42	337	338			
12:37	9.61	34	0.17	142	2800	3.40	16	19		12.6	
13:05	9.37	32	0.154	142	2800	3.40	16	18		12.6	
13:25	9.40	30	0.149	142	2800	3.40	16	16			
14:05	8.70	28	0.127	142	2800	3.40	16	15			
14:25	8.94	26	0.166	142	2800	3.40	16	14			
14:45	8.92	52	0.247	142	1400	6.49	31	29		27.7	
15:05	9.11	48	0.355	142	1400	6.49	31	26			
15:25	8.76	50	0.237	142	1400	6.49	31	27			
15:45	8.93	52	0.35	142	1400	6.49	31	29			
16:05	8.93	16	0.071	142	5000	1.94	9	9		6.1	
16:25	8.80	17	0.069	142	5000	1.94	9	9			
16:45	8.79	17	0.085	142	5000	1.94	9	9			
17:09	8.96	10	0.166	142	10000	0.99	5	5			
17:27	8.71	7	0.019	132	10000	0.99	4	4			
17:47	8.35	7	0.026	132	10000	0.99	4	4			
18:07	8.74	9	0.067	132	10000	0.99	4	5			
18:27	9.02	7	0.027	132	10000	0.99	4	4		2.1	
18:47	8.64	7	0.045	132	10000	0.99	4	4			



FIGURE 15. DGA PAN CONCENTRATION VS PAN GENERATOR  
OUTPUT DILUTION, LONG BEACH, CA, DECEMBER 1987  
**DGA PAN vs PAN Generator Output Dilution**

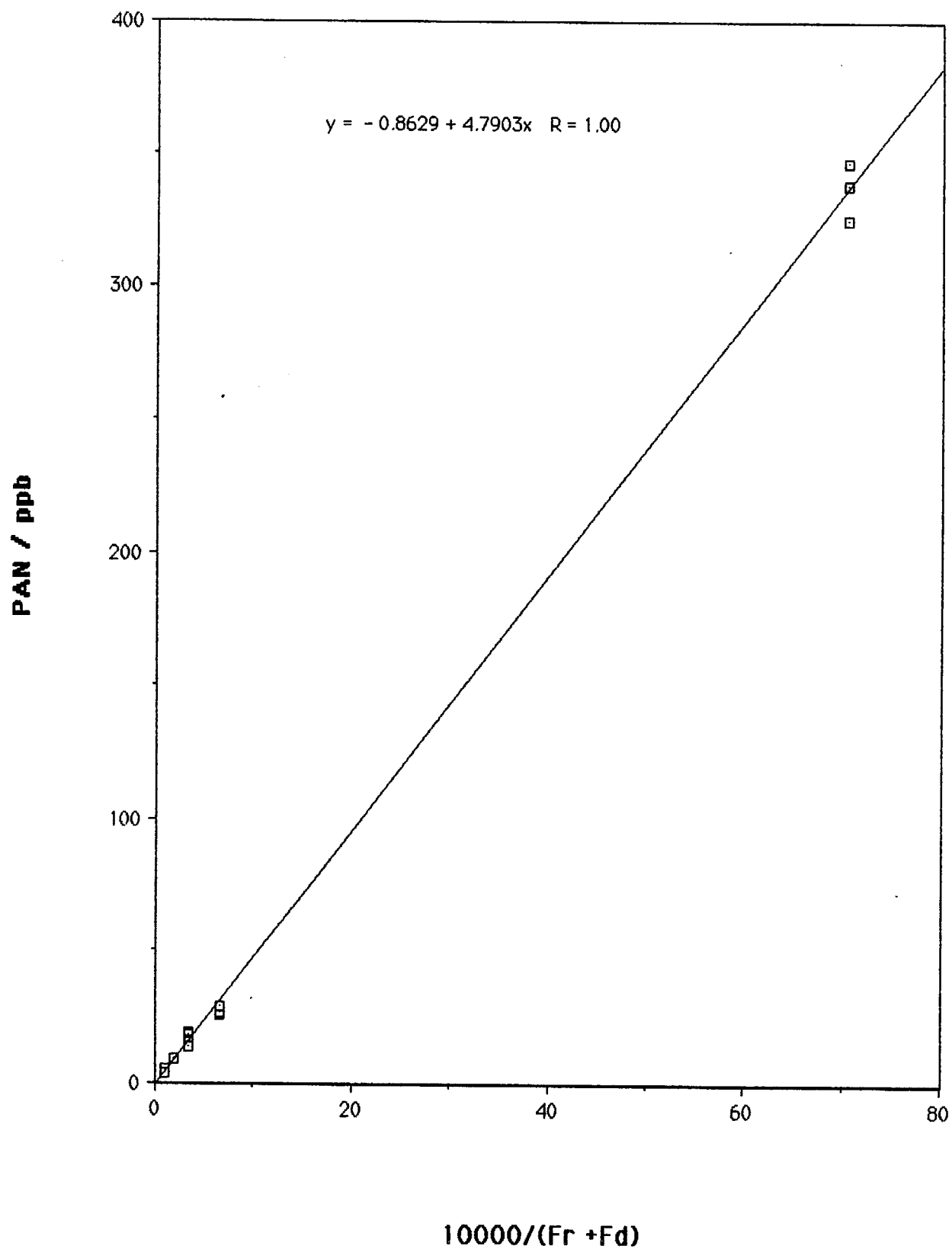
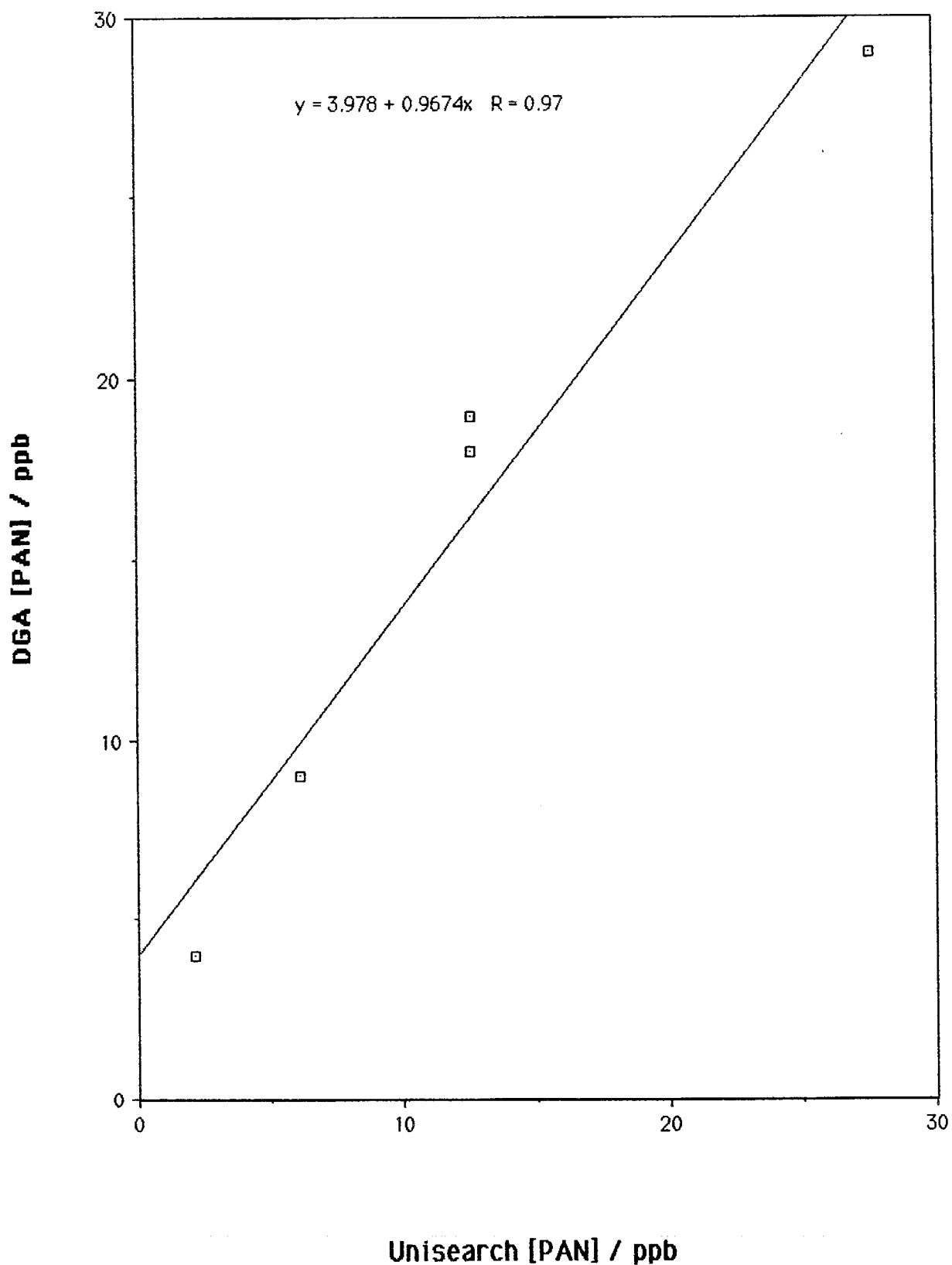


FIGURE 16. ELECTRON CAPTURE GC (DGA) AND LUMINOL  
(UNISEARCH) READINGS OF DGA PAN GENERATOR OUTPUT,  
LONG BEACH, DECEMBER 1987

**Unisearch [PAN] vs DGA [PAN]**



The second aspect of this study involves a comparison of ambient PAN measured in Long Beach by Unisearch and DGA. The Unisearch data have not been made available to us. As part of a paper presented at the National ACS Meeting last September, J. Drummond of Unisearch reported PAN levels of up to 42 ppb in Long Beach during the winter phase of SCAQS. The highest value we measured in Long Beach (see Appendix C, Data Report) was substantially lower, i.e. 15 ppb.

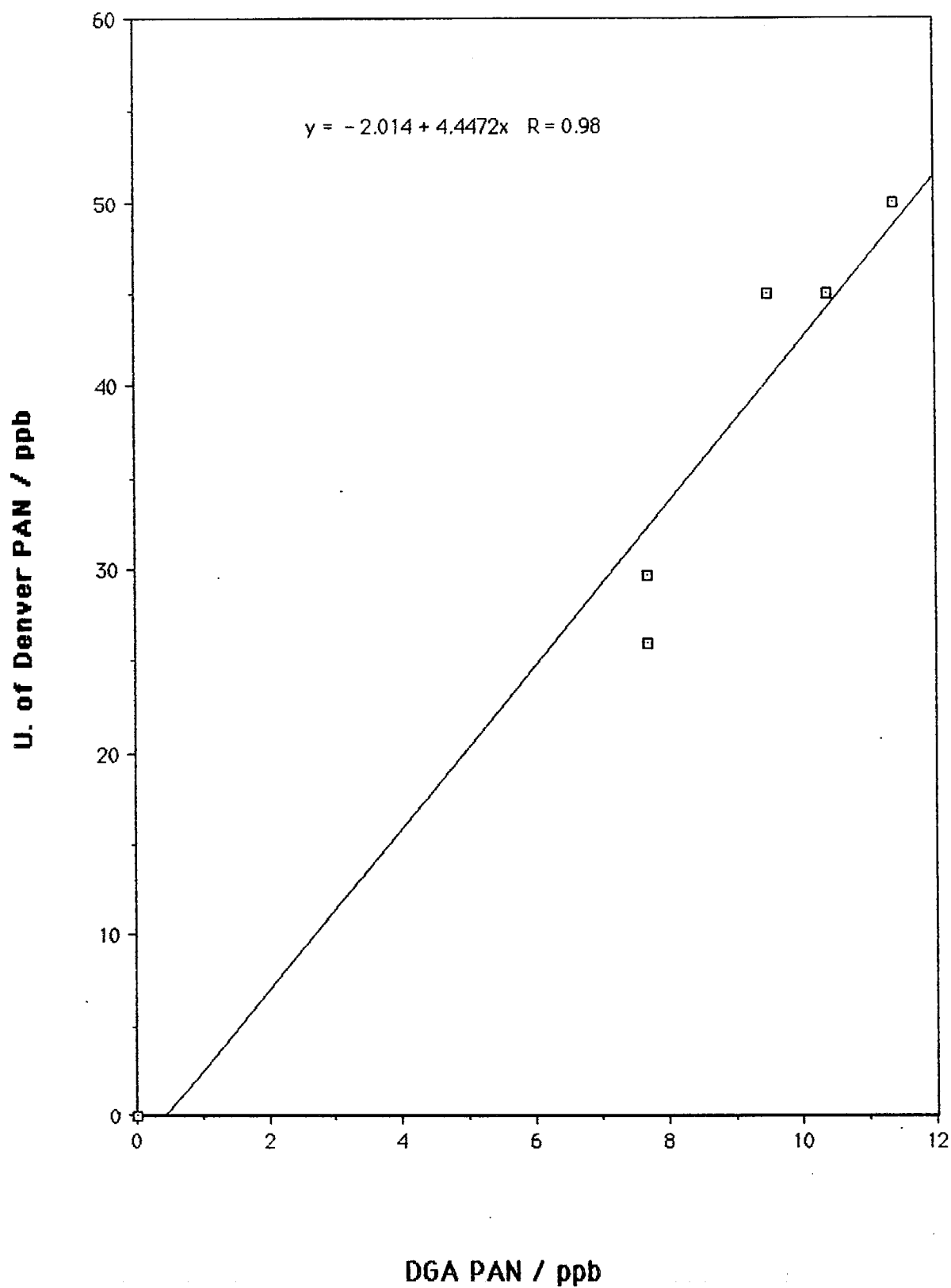
#### **5.4 Field comparison: U. of Denver and DGA**

On 6/26/87, the U. of Denver luminol instrument, which had been used to measure ambient PAN in Claremont until that time, was moved to Azusa for a brief side-by-side comparison with the DGA EC-GC instrument. The results for five ambient midday readings on a smoggy day (maximum ozone = 170 ppb) and one control (zero) sample are shown in Figure 17 and can be fit by the equation  $PAN(UD) = 4.4 PAN(DGA) - 2.0$ ,  $R = 0.98$ ,  $n = 6$ , units: ppb. Comparison should be made of the ambient Claremont PAN data reported by U. Denver, DGA and EPA to the ARB to see if a large difference also exists in the more comprehensive Claremont data set.

#### **5.5 Field comparison: GM and DGA**

The GM group carried out captive air studies, first at the Los Angeles site and later in Claremont, and measured PAN by EC-GC. They employed a standard mixture of 1 ppb of carbon tetrachloride in air as a span gas to verify instrument stability. Side-by-side readings of (a) the DGA PAN generator output at several dilutions, and (b) the GM  $CCl_4$  standard were carried out at both sites. Both instruments responded linearly to changes in PAN output dilutions.

FIGURE 17. ELECTRON CAPTURE GC (DGA) AND LUMINOL  
(U. OF DENVER) READINGS OF AMBIENT PAN, AZUSA, CA, JUNE 1987  
**EC-GC (DGA) PAN vs Luminol GC (U. of Denver)**



## 6. RESULTS AND DISCUSSION

### 6.1 PAN spatial and seasonal variations

DGA carried out some 3,500 measurements of PAN during SCAQS. Individual values are compiled in Appendix C, Data Report. A brief summary of spatial and seasonal variations in ambient PAN levels is given below.

Maximum values for each location are summarized in Table 14. Limited data for the "control" site, San Nicolas Island, indicate PAN levels of 1 ppb or less. The highest PAN concentration during SCAQS was 30 ppb and was recorded in Claremont on August 28.

Summertime maxima show a distinct increase from coastal to inland locations (Azusa, Claremont, Rubidoux). The time of the PAN maximum correspondingly shifts from about noon to mid- and late afternoon. This trend has been expected from photochemical considerations, but not demonstrated experimentally prior to this work.

Aircraft measurements, while limited, clearly indicate high levels of PAN aloft, i.e. up to 30 ppb. No prior study of PAN aloft in the SCAB atmosphere is available for comparison.

Site-to-site comparison of the summer data in Table 14 and of the corresponding ozone maxima (preliminary data obtained from SCAQMD) suggests that our data for Anaheim may be low for the period 8/27 to 9/3/88. During the same period, PAN levels were higher in Claremont than at the other two inland sites, Azusa and Rubidoux, while comparable levels of PAN were recorded at the three sites earlier in the study (6-19-7/15/88). Individual chromatograms, calibration factors, etc., were carefully verified and no discrepancy was found.

Wintertime levels of PAN were consistently high, both aloft and at ground level. On December 3, 1987, PAN maxima of 13-19 ppb were observed at all five sites. No prior data are available for comparison. The highest PAN maxima of the SCAQS winter campaign, 19 ppb in Burbank and Anaheim on December 3, are comparable to summertime maxima recorded at the inland locations. While a trend towards higher PAN values inland can be observed (Burbank had the highest PAN maxima on all six SCAQS winter sampling days), PAN levels appear more evenly distributed spatially during the winter than during the summer.

**TABLE 14. SUMMARY OF PAN MAXIMA, ppb**

Date (1987)	San Nicolas	Hawthorne	Long Beach	Anaheim	Los Angeles	Burbank	Azusa	Claremont	Rubidoux
6/19	●	ND	ND	(<4-8)	ND	ND	6	ND	ND
6/24	●	ND(<4-9)	<3-5	7	9	6	12	7	7
6/25	●	ND(<4-9)	4	6	7	5	11	5	7
7/13	1, <0-3	ND(<2-4)	3	2.3	ND	4	10	11	5
7/14	<2-4	ND	4	2.4	<7	7	4	11	9
7/15	<2-4	ND	3	1.3	ND	5	7	9	9
8/27	●	●	5	1.1	6	10	9	22	14
8/28	●	●	8	1.1	10	12	13	30	13
8/29	●	●	6	0.4	11	13	13	27	9
9/2	●	●	16	1.3	8	10	9	10	12
9/3	●	●	3	1.1	4	9	6	10	7
11/11	●	2	4	3	4	5	●	●	●
11/12	●	9	7	7	10	17	●	●	●
11/13	●	4	3	4	7	12	●	●	●
12/3	●	16	15	19	13	19	●	●	●
12/10	●	4	8	9	6	11	●	●	●
12/11	●	9	8	8	9	14	●	●	●

● PAN analyzer not operated at this site.

## 6.2 Ambient levels of methyl nitrate

Of some 3,500 ambient air chromatograms recorded during SCAQS, only seven yielded peaks that could be attributed to methyl nitrate. They are listed in Table 15 according to site, day, and time of occurrence. For all other SCAQS sites and sampling days, ambient levels of methyl nitrate were lower than our detection limit of 0.2 ppb.

Observed and calculated retention times are also listed in Table 15, where the calculated values are obtained by multiplying the observed retention time of PAN in the same air sample by a constant factor, see Section 4.2 for details.

Chromatograms of urban air samples analyzed for PAN by electron capture gas chromatography always contain peaks other than PAN. These peaks correspond mostly to chlorinated hydrocarbons. We have verified that, under the conditions we employed during SCAQS, the following compounds were well-resolved from both PAN and methyl nitrate: carbon tetrachloride, 1,1,1-trichloroethane (methyl chloroform), trichloroethylene, tetrachloroethylene, chloroform, and methylene chloride. These compounds are the most abundant halocarbons commonly present in the SCAB atmosphere.

Methyl nitrate has no known direct emission source and is produced in the atmosphere from HC-NO<sub>x</sub> reactions, PAN decomposition, and other pathways involving the CH<sub>3</sub>O + NO<sub>2</sub> reaction. While all seven observations were made during the summer phase of SCAQS at inland locations, they were also recorded at night, and the corresponding PAN concentrations were low, 0-6 ppb. Thus, there is no strong association between observations and photochemical activity. Halocarbons other than those listed above may elute at the "correct" retention time for methyl nitrate and therefore account for our observations. At any rate, methyl nitrate was not an abundant pollutant in the SCAB atmosphere during SCAQS.

## 6.3 Requested Level 2 QA

We request that Level 2 quality assurance (QA) regarding our PAN data base involve, at the minimum, the following two components:

- comparison of time series plots of PAN, NO, NO<sub>2</sub>, ozone, and temperature. Photochemical considerations indicate that high levels of PAN cannot coexist with high levels of NO, and that higher NO<sub>2</sub>/NO ratios are increasingly conducive to PAN formation and stability. The stability of

TABLE 15. POSSIBLE OBSERVATIONS OF AMBIENT METHYL NITRATE

Site	Date (1987)	Time, PST	Retention time, min		Concentration ppb(a)	PAN, ppb
			calculated(a)	observed		
AN	6/24	3:58	7.29	7.19	0.26	<6
AZ	7/12	23:18	4.8	4.65	3.2	0
	7/12	23:48	5.12	5.02	3.3	0
	7/13	0:18	5.61	5.41	4.8	0
	7/13	0:48	5.61	5.84	4.1	ND
	7/13	0:48	5.61	5.84	4.1	ND
CL	8/29	5:05	2.61	2.5	0.33	3
	8/31(b)	20:06	2.74	2.58	0.44	4

(a) as methyl nitrate. Other co-eluting compounds cannot be ruled out, see text

(b) not a SCAQS intensive day but included for completeness.



PAN is also a strong inverse function of temperature. PAN and ozone have similar precursors i.e. HC and NO<sub>x</sub>, and often exhibit similar diurnal variations. A simple comparison of the requested time series plots would help uncover inconsistencies. We have already made a preliminary and limited examination of PAN, NO, NO<sub>2</sub> and O<sub>3</sub> data for the SCAQS summer days.

- comparison of the DGA PAN data with that obtained by other SCAQS participants, i.e. U. of Denver (Claremont, June only), Unisearch (Long Beach, winter) and EPA (Claremont, summer). Of these, the comparison with the full data set obtained by EPA would be most useful, since this data set is more comprehensive and since the laboratory comparison carried out by the two groups indicated good agreement among the respective calibration methods.

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## **APPENDIX A**

### **DGA STANDARD OPERATING PROCEDURES FOR PAN MEASUREMENTS**



DGA 4  
Prepared by: EW  
Last updated by: DG  
Last Update: 11/88  
Code: PAN Measurements

## DGA STANDARD OPERATING PROCEDURES

### MEASUREMENTS OF PEROXYACETYL NITRATE (PAN)

#### 1.0 INTRODUCTION

The DGA PANalyzer is an automated gas chromatograph with an electron capture detector. The PANalyzer is used for measuring the concentration of peroxyacetylnitrate (PAN) in air. There are six main components in the PANalyzer: a gas chromatograph, an electron capture detector (ECD), an integrator, a time clock, a nitrogen supply tank and a sampling pump. Figure 1 schematically shows how these components are connected.

The PANalyzer automatically injects a 3 ml sample of ambient air into the gas chromatograph every thirty minutes. Approximately seven minutes after the injection, PAN elutes from the column and is detected by the electron capture detector.

A portable PAN generator is used to calibrate the PANalyzer. The PAN generator produces a constant concentration of PAN. Various concentrations of PAN are produced during the calibration procedure by changing the dilution air flow on the PAN generator. The operating procedure for the operation of the PAN generator is described in another SOP, number DGA-5.

#### 2.0 APPARATUS & MATERIALS

- 1) SRI Model 8610 gas chromatograph.
- 2) Valco electron capture detector.
- 3) Hitachi D-2000 Integrator, 1 V full scale.
- 4) Dayton time clock.
- 5) Hagen Optima sampling pump.
- 6) Multiple power outlet with surge and spike suppressor.

- 7) Nitrogen carrier gas cylinder: ultra high purity nitrogen must be used.
- 8) Two stage regulator with stainless steel diaphragm.
- 9) An oxygen trap (such as Oxy-Trap from Alltech) is used to remove traces of oxygen from the carrier gas.
- 10) Copper tubing, one eighth inch diameter with 1/8 inch swagelok fittings: to transfer the carrier gas from the regulator to the oxygen trap and from the oxygen trap to the gas chromatograph.
- 11) Teflon tubing, one quarter inch diameter: for the transfer of air samples to the gas chromatograph.
- 12) A 25 mm diameter in line filter holder (Nuclepore) and 25 mm diameter 1.2 micron pore size Teflon filters: to remove particulate matter from the air stream. (5 extra filters in a Petri dish)
- 13) A 24 ml vial full of a 1:1 CH<sub>3</sub>OH: H<sub>2</sub>O solution and a medicine dropper for leak testing the GC.

### 3.0 PROCEDURE

#### 3.1 INITIAL-SET UP

- 1) Connect the copper tubing used as carrier gas line to the regulator.
- 2) Using the regulator, turn nitrogen carrier gas on.
- 3) Purge the copper tubing with nitrogen for about one minute. Copper tubing not previously used as carrier gas line should be cleaned by heating with a heat gun for a few minutes while the tubing is being purged with nitrogen.
- 4) With the nitrogen still on, connect the carrier gas line to the oxygen trap.
- 5) Connect a second piece of copper tubing to the other end of the oxygen trap. Purge this tubing with nitrogen for about one minute and clean as in #3 if this is new tubing.

- 6) Connect the other end of the tubing to the GC. Make sure that the 1/8" swagelok cap has been removed from the carrier gas exit on the GC.
- 7) Make sure that the appropriate PAN column is installed in the GC. Note: brass swagelok ferrules should be used when installing Teflon columns.
- 8) Set the cylinder regulator to the value indicated in the PAN analyzer log book (50-100 psig).
- 9) Adjust the GC column pressure regulator to the value indicated in the PAN analyzer log book (8-20 psig). Measure the column flowrate. The carrier gas flowrate through the column is measured by disconnecting the detector side of the column and then connecting a bubble flowmeter to the end of the column. Record the nitrogen flowrate through the column. Let nitrogen carrier gas purge the system for about thirty minutes. Steps 10-16 may be completed while the system is being purged with nitrogen.
- 10) Leak test all connections with a 50:50 (vol.%), water: methanol solution.
- 11) Connect the Teflon transfer line to the particulate filter holder and then to the sample inlet of the gas chromatograph.
- 12) Connect the loop exit on the gas chromatograph to the Hagen Optima pump with 1/8" Teflon tubing.
- 13) Connect the Valco ECD to the gas chromatograph. Make sure that the anode and cathode cables are correctly connected.
- 14) Connect the integrator to the gas chromatograph. Use the ground cable to ground the integrator if possible.
- 15) Connect GC, ECD, integrator, timer and pump to power outlet through a surge suppressor.
- 16) Open the red cover of the PANalyzer and turn on the power to the gas chromatograph and the integrator. The power switches are on the left side of the gas chromatograph and on the top of the integrator.

- 17) Turn on the detector heater and set it to  $-60^{\circ}\text{C}$ .
- 16) Turn the knob on the right front of the GC to the "Setpoint" position and check to see if the digital display on the front panel of the GC reads as indicated in the PAN analyzer log book (32-35). If the display does not read as it should, then it is necessary to adjust the setpoint. To do this, first, lift the red cover. Second, adjust the initial setpoint screw located on the top right front quadrant of the GC until the digital display reads correctly.

Turn the above mentioned knob to the "Actual" position. (Note: the digital display on the front of the GC does not display the actual temperature.)
- 19) After the detector is at  $60^{\circ}\text{C}$ , indicated by a blinking yellow light, close the red cover and allow the oven to regulate the temperature. A blinking red light on the GC indicates that the temperature of the oven is being properly regulated.
- 20) Load parameter file 1 into the integrator and set the date and time. The initial method development file which should be stored in parameter file 1 is listed in Appendix I.
- 21) Connect the Dayton timer to the GC injection valve and the Hitachi integrator. Make sure that the time clock is correctly triggering the GC injection valve and the integrator. If the timer is triggering the equipment in reverse order, then the wire connections on the timer connected to the normally open and normally closed terminals need to be interchanged. BE SURE TO UNPLUG THE TIMER BEFORE CHANGING ANY WIRES.
- 22) If the PANalyzer is to be operated now, proceed with the next step, otherwise follow the PANalyzer shut down or PANalyzer standby procedures.
- 23) After about 20 minutes press the start button on the integrator and monitor the baseline. The baseline should not drift more than 15% of fullscale in one hour and the noise should be less than 2% of full-scale. Excessive noise or drift indicates a possible air leak or contamination of the carrier gas. Continue purging the system with carrier gas for several hours. If there is still a problem, refer to the instrument manual for troubleshooting and contact the project manager.



- 24) When the system is ready, start the Hagen pump and wait five minutes before proceeding.
- 25) Connect the gas chromatograph and the integrator to the time clock and plug in the time clock to start automatic PAN analysis.
- 26) Observe the peaks on the integrator. In a typical ambient air chromatogram, a large (offscale) peak due to oxygen in the air sample appears first, followed by the PAN peak in about 7-15 minutes. Occasionally other peaks are present, e.g. fluorocarbons, chlorinated hydrocarbons, methyl nitrate.

### 3.2 DAILY TASKS

- 1) Tasks to be performed daily are listed in the attached SHORT DAILY CHECKLIST and LONG DAILY CHECKLIST. The short daily checklist includes recording of the baseline voltage on the BASELINE voltage LOG SHEET, and spells out emergency shut off procedures. One copy each of the SHORT DAILY CHECKLIST and of the BASELINE voltage LOG SHEET are taped on wall nearest to PAN analyzer. The LONG DAILY CHECKLIST forms are included, along with instrument manuals and a copy of this SOP, in the log-book kept with each PAN analyzer unit.
- 2) It is important that the amount of N<sub>2</sub> left in the carrier gas tank be monitored daily to make sure that it is not being used excessively fast. Rapid consumption of nitrogen may indicate leaks, please leak-check. A new tank should be installed when the tank pressure drops to ~300 psig.
- 3) The Teflon filter in the sampling line should be replaced every three days of operation. A new Teflon filter is white in appearance. Make sure that the colored plastic spaces between the Teflon filters in the storage box are not inserted in the Teflon filter holder.

### 3.3 STANDBY PROCEDURE FOR DGA PAN ANALYZERS

See the attached Standby Procedure. A copy of the Standby Procedure is taped to the wall near the PAN analyzer.

### 3.4 SHUT DOWN OF THE PAN ANALYZER

- 1) Disconnect the time clock from the gas chromatograph and the integrator.
- 2) Unplug the sampling pump
- 3) Open the red cover of the PANalyzer and remove the aluminum lid from the oven.
- 4) Turn off the ECD.
- 5) After the oven has cooled to 28 turn off the ECD heater.
- 6) Turn off the gas chromatograph and the integrator.
- 7) Make sure that the injection valve in the GC is turned off by looking at the toggle switch used in making manual injection. If the indicator light is off then the valve is off. Unplug the injection valve if the indicator light is still on.
- 8) Disconnect the GC side of the oxy-trap from the carrier gas line and plug the Oxy-trap with a swagelok cap.
- 9) Turn off the N<sub>2</sub> carrier gas with the tank valve.
- 10) Cap the GC vent and carrier gas entrance with 1/8" swagelok caps.

### 3.5 Start up of the PAN analyzer after the carrier gas has been turned off

- 1) Remove the 1/8" swagelok caps from the carrier gas entrance and vent.
- 2) Turn on the N<sub>2</sub> carrier gas and set the regulator according to the PAN Analyzer log sheet.
- 3) Uncap the GC side of the Oxy trap and connect it to the GC.

- 4) Follow step 9 in the Initial Setup Procedure.
- 5) Allow the carrier gas to purge the system for thirty minutes.
- 6) Measure and record the total flowrate through the GC. To do this, connect the bubble flowmeter to the vent on the left side of the GC.
- 7) Follow steps 10 and 16 through the end of Section 3.1. Initial Start Up Procedure.

### 3.6 ATTACHMENTS AND LOG SHEETS

Figure 1. DGA PAN analyzer

Appendix 1: Integrator parameter file

Short daily checklist (includes emergency shut off procedures)

Baseline voltage log sheet

Long daily checklist

Standby Procedure for DGA PAN Analyzers

### 4.0 PREPARATION OF PAN DATA REPORTS

#### 4.1 INTRODUCTION

Peroxyacetylnitrate (PAN) is measured using an electron capture gas chromatograph. The output, called chromatogram, is recorded on a Hitachi D-2000 electronic integrator. The chromatogram thus recorded includes several peaks, one of which is PAN. The PAN peak has been positively identified by:

- \* observing its disappearance when removing PAN from the air stream using an alkaline trap (other peaks e.g. oxygen, halocarbons, water, are not affected by the trap).
- \* verifying that its retention time, obtained under identical conditions, matches that of an authentic sample of PAN prepared with the DGA PAN generator.

The task at hand consists of compiling PAN peak heights from the chromatograms onto a Microsoft EXCEL spreadsheet, and to enter the appropriate factor to convert peak heights to PAN concentrations in parts per billion (ppb).

## 4.2 COMPILATION OF PEAK HEIGHTS

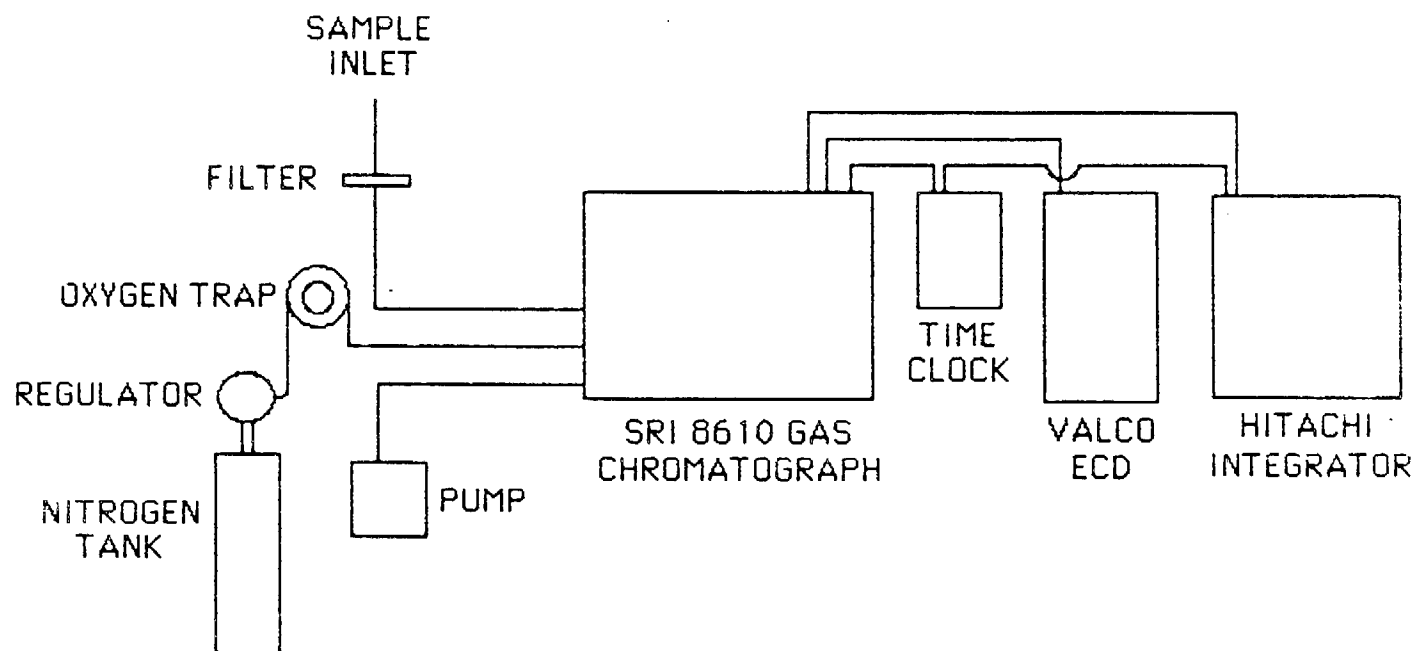
- 4.2.1 Using a Microsoft EXCEL spreadsheet (MacIntosh Plus), create a table with vertical columns and the following entries: DATE, TIME, PEAK HEIGHT, PAN PPB, AND COMMENTS.
- 4.2.2 Organize rolls of chart paper by sampling site and by chronological order. Set up one spreadsheet table for each sampling site. Use the sampling site name or code as the title for each table (e.g. LONG BEACH).
- 4.2.3 Draw a baseline for the PAN peak with the ends of the baseline centered in the noise surrounding the PAN peak. Measure in mm the peak height in the center of the PAN peak in each consecutive chromatogram. Enter date, time and peak height in the corresponding columns on the spreadsheet. Proceed until PAN peak heights have been entered on log sheet for all chromatograms for a given sampling site.
- 4.2.4 Enter the conversion factor (obtained from Daniel Grosjean or Edwin Williams) for this sampling site (do not assume that the same conversion factor applies to all sites).

## 4.3.0 DATA CHECKS

- 4.3.1 Verify from sampling log sheets that detector and integrator settings have remained constant throughout the sample data base. If in doubt, enter in COMMENTS column of spreadsheet.
- 4.3.2 Verify, on every other chromatogram, that the retention time of the PAN peak is constant throughout the study. If in doubt, consult DGA project manager and enter in COMMENTS column of spreadsheet.
- 4.3.3 Verify, on each chromatogram, that the PAN peak did not overlap with other peaks. Enter any observed overlap in the COMMENTS column.
- 4.3.4 Repeat step 4.3 on ten percent of the chromatograms taken at random.
- 4.3.5 Discuss all discrepancies and problem areas with DGA project manager.

- 4.3.6 Re-roll chromatograms, clearly label the outside of the roll with project title (e.g. SCAQS), sampling site (e.g. LONG BEACH) and data span (e.g. FROM JUNE 25, 1987, 12:03 PDT TO JUNE 28, 1987, 15:23 PDT). Return rolls to DGA project manager for filing.

# DGA PAN ANALYZER



# APPENDIX 1

FILE NO. = 3

## DATE TITLE

DATE & TIME = 06/10/87 16:31  
TAG NO. = 22  
METHOD NAME = PAN TEST

## SAMPLING PERIOD : SEMI-AUTO

NO.	TIME	PERIOD
1	0.00	800
2	20.00	1600
3	60.00	3200

## REPORT PLOT : CHROMATO&DATA

CHART SPEED = 1.25  
PLOT ATT = 3  
CHROMATO OFFSET = 10  
BASE ANALYSIS = BASELINE  
PEAK LABEL = TIME  
OVERLAPPED PEAK = ALL  
TIME SCALE PLOT = YES  
TIME PROG. MARK = YES  
AUTO RECALC = YES  
COMMENT AUTO = NO  
CONC UNIT = CONC

## PRINT FORMAT :

NO.	RT	AREA	CONC	BC
-----	----	------	------	----

## TIME PROGRAM

TIME	FUNC	VAL/STATUS
0.00	SENS	4
0.00	AUTO ZERO	ON
25.00	STOP	ON

CALC METHOD = AREA% : AREA  
PEAK REJECTION = 2000  
DATA JUDGEMENT = NONE

## SPEC. MODES

SAMPLER TABLE = OFF  
LINK TABLE = OFF  
SPEC.ANAL. MODE = NONE

## PAN ANALYZER SHORT DAILY CHECKLIST

1. If there is less than 500 psig of nitrogen in the tank notify DGA.
2. Make sure the chart paper does not accumulate over the integrator.
3. If the chart paper jams or runs out notify DGA.
4. Record the baseline voltage several times a day on the PAN ANALYZER Baseline Voltage Log Sheet.

IF THE NITROGEN PRESSURE ON THE FIRST STAGE OF THE TANK  
REGULATOR IS 100 psig OR LESS TURN OFF THE GC IMMEDIATELY AND  
THEN NOTIFY DGA.

Day: (805)644-0125  
Night: (818)244-5053  
Machine: (805)482-5330

## EMERGENCY GC SHUTOFF PROCEDURE

1. Turn off the toggle switch on the bottom left corner of the brown ECD control unit.
2. Lift the red cover of the ECD. Warning: cover may be hot!
3. Turn off the ECD Temperature control knob located above the toggle switch on the ECD control unit.
4. Notify DGA immediately.



# PAN ANALYZER

# BASELINE VOLTAGE LOG SHEET

LOCATION: \_\_\_\_\_

[illegible]

## PANANALYZER LONG DAILY CHECKLIST

Last Update: 11/87

Location: \_\_\_\_\_

IF THE NITROGEN PRESSURE ON THE FIRST STAGE OF THE REGULATOR IS 100 psig OR LESS TURN OFF THE GC IMMEDIATELY

Please check the following items and record the appropriate information or a check mark to the right.

1. Date				
2. Time				
3. Record the Baseline Voltage				
4. Read the PAN Analyzer Baseline Voltage Log Sheet that the AV personnel have made and record the time and baseline voltage to the right as time/voltage				
5. Record the pressure on the first stage of the Nitrogen tank regulator				
6. Record the pressure on the second stage of the Nitrogen tank regulator				
7. Record the value of the pressure on the gauge located in front of the GC				
8. Record ECD Baseline Adjust Setting				
9. Record ECD Attenuation				
10. Record ECD Temperature Setting				
11. Record the GC Digital Display Reading (with the right knob in the "Actual" position)				
12. Check to see if the teflon filter in the sampling line is dirty. If the filter is dirty, change it and record the date to the right. (The filter should be changed at least once in each intensive period)				
13. Make sure that the sampling line entrance points toward the ground.				
14. Make sure the chart paper does not accumulate over the integrator				
15. Make sure the chart paper does not jam				
16. Check the amount of chart paper left and try to estimate when the paper will need to be changed. Change the chart paper if necessary				
17. Check for a blinking red light on the left corner of the GC.				
18. Check for a blinking yellow light on the ECD control unit				
19. Check the time printed on the chromatograms and initial the time if it is the correct Pacific Standard Time, PST, for the injection. If the time is incorrect: 1) record the correct PST for the last injection on the chromatogram next to the incorrect time and 2) reset the integrator to the correct PST and date.				
20. Phone information to Ed Williams: Day: (805)644-0125; Night: (818)244-5053; Machine: (805)482-5330				

STANDBY PROCEDURE FOR DGA PAN ANALYZERS  
(Last update: 5/88)

1. Identify time clock (Dayton timer): a book-sized grey box that resembles a hi vol timer or a swimming pool timer.
2. SHORTLY AFTER SCAQS "GO" DAY:
  - 2.1 Unplug time clock. Do NOT unplug or switch off any other component of the DGA analyzer, only the time clock.
  - 2.2 To verify that time clock is OFF, open front door of timer and watch the yellow wheel for 2-3 minutes; the wheel should no longer rotate.
  - 2.3 NOTE: After the time clock has been unplugged, the Hitachi integrator may continue to acquire data for up to 30-45 minutes. This is OK. Do NOT switch the integrator off.
3. ON THE EVENING OF A GO DAY (Around 9 p.m.)
  - 3.1 Plug time clock into power outlet.
  - 3.2 To verify that time clock is ON, open front door of timer and watch the yellow wheel for 2-3 minutes: the wheel will start moving, making a full rotation in 60 minutes.
4. THANK YOU

# PAN RETENTION TIMES VERIFIED IN THE FIELD USING THE PAN GENERATOR

Location	Date	PAN retention time, min.	
		from PAN generator (a)	from ambient air measurements (a) (b)
Anaheim	9/16	12.2 ± 0.3	12.0 ± 0.2
Azusa	6/26-6/29	18.53 ± 0.58	16.70 ± 2.38
Burbank	7/21	10.8 ± 0.2	9.96 ± 0.72
Claremont	8/26-8/27	8.59 ± 0.24	8.52 ± 0.51
Claremont (Seavers Hall)	9/9-9/10	7.55 ± 0.11	7.29 ± 0.34 (c)
Long Beach	7/23	12.52 ± 0.13	12.49 ± 0.16
Long Beach	12/14	8.89 ± 0.32	8.99 ± 0.78
Los Angeles	7/2-7/5	26.11 ± 0.52	25.36 ± 2.05
Rubidoux	7/31	20.97 ± 1.38	22.4 ± 1.45

(a) All uncertainties are one standard deviation.

(b) Average PAN retention time for the group of SCAQS "go days" nearest to the date of the PAN generator verification.

(c) Average PAN retention time for 9/9-9/10.

## **APPENDIX B**

### **ERROR ANALYSIS**

## INTRODUCTION

The uncertainties in reported PAN concentrations have been estimated with a standard error propagation analysis. Uncertainties range from 51% at the lowest PAN concentrations to 12% at the highest PAN concentrations, with typical values in the range of 14 to 19%. The error analysis is divided into the following two sections: uncertainty in calibration of the reference GC, and uncertainty in field measurements.

### Uncertainty in calibration of the reference GC

#### Overview

The relative uncertainty in the reference GC calibration factor was estimated to be 4.2% (calibration factor =  $0.2224 \pm 0.0094$  ppb  $\text{mm}^{-1}$ ). This uncertainty is related to the uncertainties in the absolute PAN concentrations (measured by  $\text{NO}_x$  chemiluminescence, section 4.1.5, and alkaline decomposition of PAN to acetate, section 4.1.4.) and to the accuracy of the statistical model used to fit the data. The following sections present a standard propagation of error analysis for the chemiluminescence and alkaline hydrolysis methods and describe the justification for the use of a weighted least squares forced through the origin.

#### Propagation of errors for the chemiluminescence method

The chemiluminescence method is described in section 4.1.5. The formula for calculating PAN concentrations is as follows:

$$\text{PAN} = A - B/(1 - C)$$

where A and B are the ( $\text{NO}_x$ -NO) concentrations measured upstream and downstream of the alkaline cartridge, respectively, and C is the fraction of  $\text{NO}_2$  removed by the cartridge. Uncertainty in the PAN concentration is given by:

$$\sigma_{\text{PAN}}^2 = \sigma_A^2 + \sigma_B^2 \left( \frac{1}{1 - C} \right)^2 + \sigma_C^2 \left( \frac{B}{(1 - C)^2} \right)^2$$

The parameters  $\sigma_A$  and  $\sigma_B$  are estimated to be  $\pm 2$  ppb from the uncertainty in calibration and stability of the chemiluminescent analyzer. The amount of  $\text{NO}_2$  removed by the alkaline cartridge was measured in separate experiments with  $\text{NO}_2$  in pure air and is given by:

$$C = \frac{x - y}{x}$$

where  $x$  and  $y$  are the  $\text{NO}_2$  measured upstream and downstream of the cartridge, respectively. The corresponding uncertainty is given by:

$$\left(\frac{\sigma_c}{C}\right)^2 = \left(\frac{\sigma_x}{x}\right)^2 + \left(\frac{\sigma_y}{y}\right)^2$$

Uncertainties in  $x$  and  $y$  were estimated from the scatter in experimental data to be  $\pm 2$  and  $\pm 6$  ppb, respectively. Table B-1 lists the PAN concentrations and their estimated uncertainties for both chemiluminescence and acetate calibration points.

#### Propagation of errors for alkaline hydrolysis method

PAN concentrations were measured by collecting air samples containing PAN on alkaline impregnated cartridges. The cartridges were eluted and analyzed for acetate by HPLC with ultraviolet detection (see Section 4.1.4). Uncertainties in PAN concentrations are due to the uncertainty in the collection and analysis of the alkaline cartridges.

Uncertainties in acetate concentrations were attributed to errors in the HPLC calibration, the sample injection volume and the measurement of peak heights. To calibrate the HPLC, known acetate concentrations are injected and a plot of acetate in  $\mu\text{g}$  versus peak height in  $\text{mm}$  is constructed. One of the two HPLC calibration plots used is shown in Figure B1. The slope,  $S$   $\text{mm } \mu\text{g}^{-1}$ , and the intercept,  $I$   $\text{mm}$ , are calculated by fitting the data with an unweighted linear regression line. Unknown

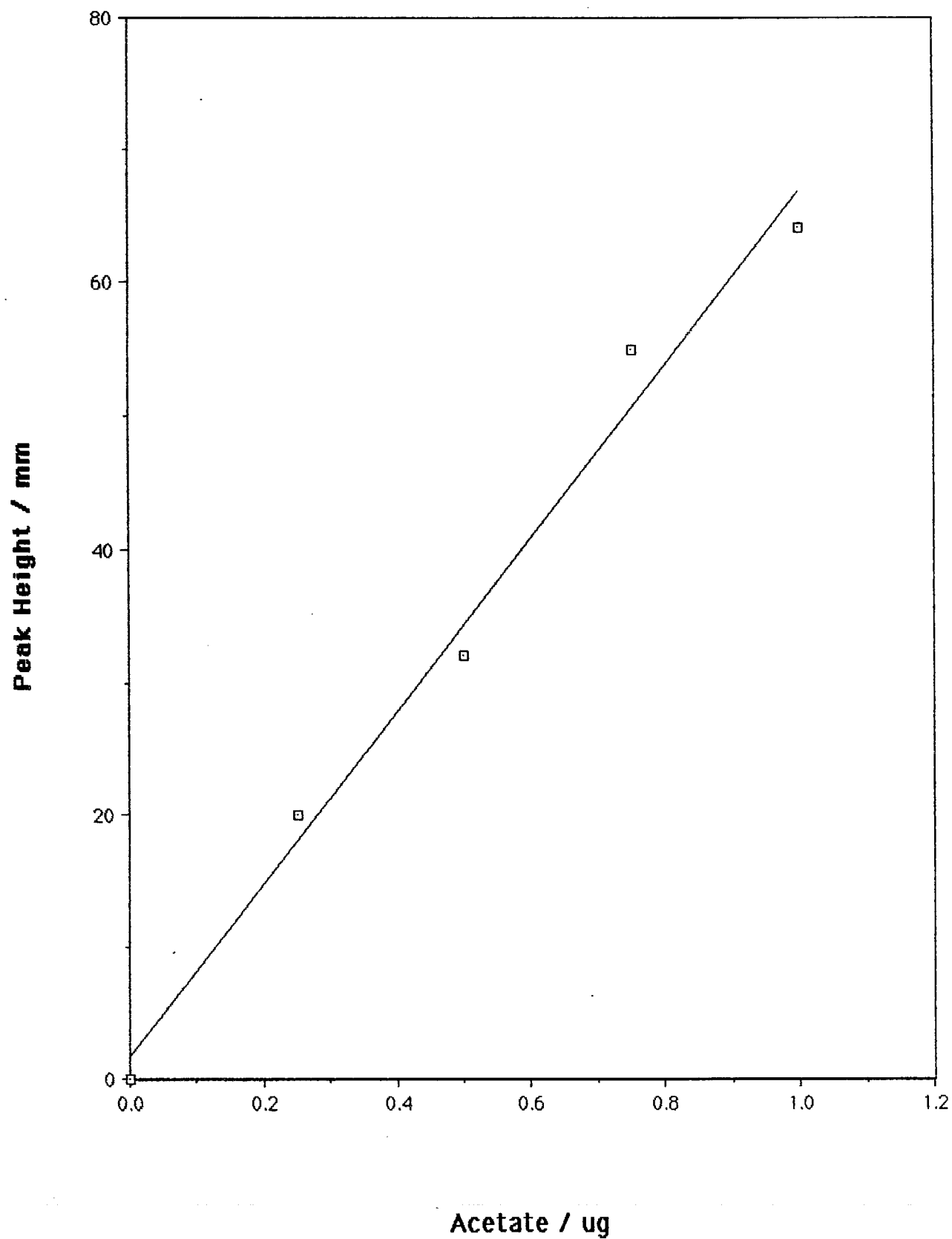
TABLE B-1. REFERENCE GC PAN CALIBRATION DATA

Method	Peak Area, 10 <sup>5</sup> counts	Peak Height, mm	Acetate, μg/ml	Collection time, min.	Flow, ml/min	PAN, ppb
Chemiluminescence	0.369	132				28.2 ± 3.3
Chemiluminescence	0.279	108.5				27.5 ± 3.3
Chemiluminescence	0.216	94.8				14.4 ± 3.3
Chemiluminescence	0	0				0 ± 2
Acetate	2.99	1032	8.5 ± 0.91	301	106	223 ± 32
Acetate	4.15	1279	2.37 ± 0.168	74	96	278 ± 35
Acetate	4.27	1266	2.64 ± 0.182	74	96	310 ± 39
Acetate	2.30	688	1.90 ± 0.103	120	101	131 ± 15
Acetate	1.43	528	1.44 ± 0.095	90	101	132 ± 16
Acetate	2.02	680	2.70 ± 0.088	120	101	186 ± 19



Figure B-1

# HPLC Calibration Plot for Acetate, Feb. 1988



acetate samples are injected into the HPLC and the acetate concentration is calculated from the injection volume, V in ul, and the analyte peak height, PH in mm, as follows:

$$Ac, \text{ ug mL}^{-1} = \frac{1000 (PH - I)}{V * S}$$

where Ac is the acetate concentration and the constant is used for unit conversion. The uncertainty in the unknown acetate concentration is given by:

$$\begin{aligned} \sigma_{Ac}^2 = & (\sigma_I^2 + \sigma_{PH}^2) \left( \frac{1000}{V * S} \right)^2 + \sigma_V^2 \left( \frac{1000 (PH - I)}{V^2 * S} \right)^2 \\ & + \sigma_S^2 \left( \frac{1000 (PH - I)}{V * S^2} \right)^2 \end{aligned}$$

Estimated uncertainties in the peak height and 100 ul injection volume are  $\pm 1$  mm and  $\pm 2$  ul, respectively. One standard deviation of the slope and intercept from the acetate calibration plot were used to estimate  $\sigma_S$  and  $\sigma_I$  respectively.

PAN concentrations are calculated as follows:

$$PAN, \text{ ppb} = \frac{8.33 * 10^5 * Ac}{F * t}$$

where F is the flow through the alkaline cartridge in  $\text{ml min}^{-1}$ , t is the collection time in minutes and the constant is used to convert the units to ppb. The uncertainty in the PAN concentration is given by:

$$\left( \frac{\sigma_{PAN}}{PAN} \right)^2 = \left( \frac{\sigma_{Ac}}{Ac} \right)^2 + \left( \frac{\sigma_F}{F} \right)^2 + \left( \frac{\sigma_t}{t} \right)^2$$

Estimates of 10 ml min<sup>-1</sup> and 0.5 minute are used for the uncertainties in F and t, respectively. PAN concentration uncertainties calculated from the above equations are given in Table B-1.

#### Selection of least squares fit to data

Analysis of the theory of a least squares fit of data to a straight line (Bevington, 1969) has prompted us to select a weighted least squares program as the most appropriate method to fit our calibration data. A regression fit of data to a straight line assumes that all the uncertainties have been assigned to the dependent variable alone. In the case of the reference GC calibration, the uncertainties in the independent variable (peak area or peak height) can be ignored because they are much lower than the uncertainty in the PAN concentration. A regression fit of data can be either unweighted, where the absolute uncertainties in the dependent variables are equal, or weighted when these uncertainties are unequal. Since the uncertainties in PAN concentrations were unequal, (See Table B-1), a weighted regression fit was applied to our calibration data.

#### Regression analysis

Results of weighted least squares fitting of the calibration data given in Table B-1 are summarized in Table B-2. Peak height and peak area calibration factors were calculated in two ways: computing the intercept or forcing the intercept through zero. Columns one and two of Table B-2 show results for separate regression analysis of the chemiluminescence and alkaline hydrolysis data points, respectively. Within experimental uncertainty, identical slopes were obtained for the two sub-sets of data. Thus, the two data sub-sets belong to the same parent population and were combined for calibration of the reference GC.

#### Forcing through origin

In theory the intercept of the reference GC calibration curve should be zero. Experimental data agree with theory: in numerous control measurements carried out in this laboratory with purified air (no PAN present), the acetate blanks were near our detection limit, the NO<sub>x</sub> analyzer measured 0 - 2 ppb and the GC recorded no measurable peak height (or peak area). Therefore, any deviation from a zero intercept in the calibration is most likely due to the sparsity of calibration data. If

the intercept is not forced through zero, the relative accuracy of reported PAN concentrations would decrease with the concentration. Results in Table B-2 indicate that the experimental data fit the model well with the computed intercept equal to zero within one-half ppb. To calculate as accurate as possible a calibration factor, we elected to force the intercept through zero. Table B-2 shows that the standard error in the slope of the peak height data was about the same whether or not the intercept was forced through zero.

#### Least squares through the origin equations

A linear least squares computer program was modified so that it would force the intercept of the fitted line to be zero. A brief derivation of the equations used in the program is given below. The equation of the lines is given by:

$$y = A_0 + A_1x$$

where  $A_0$  is the intercept and  $A_1$  is the slope. Chi-square was minimized, after setting the intercept equal to zero.

$$\chi^2 = \sum \frac{1}{\sigma_i^2} (y_i - A_1 x_i)^2$$

$$\frac{\partial \chi^2}{\partial A_1} = \sum \frac{-2x_i}{\sigma_i^2} (y_i - A_1 x_i)^2 = 0$$

$$A_1 = \frac{\sum \left( \frac{x_i y_i}{\sigma_i^2} \right)}{\sum \left( \frac{x_i^2}{\sigma_i^2} \right)}$$

TABLE B-2. WEIGHTED LEAST SQUARES FIT TO REFERENCE GC CALIBRATION DATA

Calibration Method	Chemiluminescence	Alkaline hydrolysis	Both	Both	Both	<b>Both</b>
intercept	zero	zero	compute	compute	zero	<b>zero</b>
dependent variable	peak height	peak height	peak area	peak height	peak area	<b>peak height</b>
number of points	4	7	10	10	10	<b>10</b>
slope	0.2114	0.2273	73.62	0.2235	74.14	<b>0.2224</b>
Std. error of slope	0.0169	0.0112	3.29	0.01	3.14	<b>0.0094</b>
intercept	0	0	0.47	-0.304	0	<b>0</b>
Std. error of intercept	n/a	n/a	0.92	0.9349	n/a	<b>n/a</b>
R	0.981	0.992	0.983	0.988	0.983	<b>0.988</b>

n/a = not applicable

The uncertainty in the slope was found with the use of the following equation, as recommended by Bevington. (Bevington, 1969).

$$\sigma_{A1}^2 = \sum \left[ \sigma_i^2 \left( \frac{\partial A1}{\partial y_i} \right)^2 \right]$$

$$\sigma_{A1}^2 = \sum_{j=1}^N \left[ \sigma_j^2 \left( \frac{x_j (1/\sigma_j^2)}{\sum (x_i^2/\sigma_i^2)} \right)^2 \right]$$

$$\sigma_{A1}^2 = \frac{1}{\sum (x_i^2/\sigma_i^2)}$$

#### RELATIVE UNCERTAINTY IN FIELD MEASUREMENTS

Relative uncertainties in reported PAN concentrations depend on peak height and on the relative uncertainty in the specific calibration factor for each instrument. The instrument specific calibration factor,  $C_x$ , is calculated from the reference GC peak height calibration factor,  $C_2$ , and the relative response factor  $R_2$  as follows:

$$\frac{1}{R_2} * C_2 = C_x$$

$$R_2 = \frac{PH}{PHR}$$

where  $PH$  and  $PHR$  are the PAN peak heights on the GC being calibrated and on the reference GC, respectively. Combining the two equations given above, the uncertainty in  $C_x$  is given by:

$$\left( \frac{\sigma_{C_x}}{C_x} \right)^2 = \left( \frac{\sigma_{C_2}}{C_2} \right)^2 + \left( \frac{\sigma_{PH}}{PH} \right)^2 + \left( \frac{\sigma_{PHR}}{PHR} \right)^2$$

The uncertainty in C2 is the standard error in the slope of the reference GC calibrations curve, 0.0094. Rather than calculating the relative uncertainties in the peak heights for each GC an estimate is made of their uncertainties which could be used for all GC comparisons. To do this, it is assumed that the relative uncertainties in the peak heights measured on all gas chromatographs are equivalent:  $(\sigma_{PHR}/PHR) = (\sigma_{PH}/PH)$  DGA 52 =  $(\sigma_{PH}/PH)$  DGA 53 etc.). Next, the means and standard deviations of all relative peak height uncertainties are calculated from experimental data,  $\sigma_{PH/PH} = 0.0267 \pm 0.0213$ . To arrive at a reasonable estimate for the relative peak height uncertainty which applies to all GCs, two standard deviations are added to the above mean value, i.e.  $\sigma_{PH/PH} = 0.0693$ . The relative uncertainty in  $C_x$  is calculated from above to be 0.098.

PAN concentrations and their relative uncertainties are calculated from the following equations:

$$PAN = PH * C_x$$

$$\left( \frac{\sigma_{PAN}}{PAN} \right)^2 = \left( \frac{\sigma_{PH}}{PH} \right)^2 + \left( \frac{\sigma_{C_x}}{C_x} \right)^2 + 2 \sigma_{C_x PH}$$

The relative errors in the PAN peak heights in the field chromatograms are due to the error in their physical measurement,  $\pm 1$  mm, and the uncertainty in their reproducibility,  $\pm 2\%$  (Section 2.1.5).

Errors in the peak height and in the calibration factor are correlated because there is an incremental change in the peak height calibration factor for every incremental change in the PAN retention time. In the field the PAN retention times for any GC varied on average by  $\pm 10\%$ . A laboratory experiment was conducted in which a constant concentration of PAN, 28 ppb, was injected into the same GC while the PAN retention time was deliberately varied by changing the carrier gas flow rate. Figure B-2 shows that a 10% change in retention time would corresponds to a 4.5% change in peak height. Therefore, the uncertainty due to the correlation between peak height and calibration factor was estimated to be 4.5%. The relative uncertainty in the PAN concentration as a function of peak height is given in Table B-3.

FIGURE B-2. Retention Time vs Peak Height; [PAN] = 28 ppb

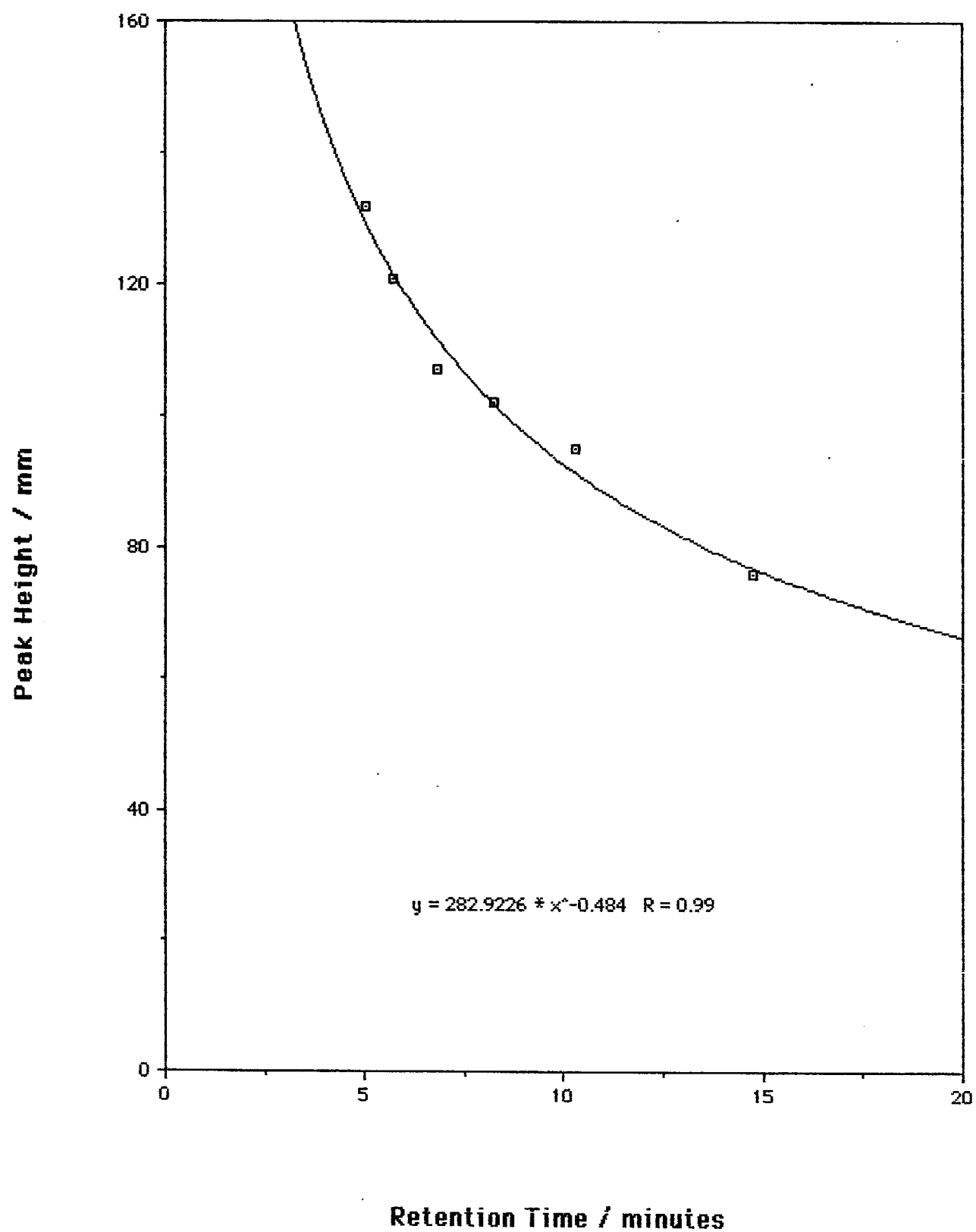




TABLE B-3. RELATIVE UNCERTAINTY VS. PEAK HEIGHT IN PAN FIELD MEASUREMENTS

Peak Height, mm	pan/PAN
1	1.00
2	0.51
3	0.35
4	0.28
5	0.23
7	0.19
10	0.15
15	0.14
20	0.13
25	0.12
30	0.12
40	0.12
80	0.12

## ABSOLUTE UNCERTAINTY IN FIELD MEASUREMENTS

The absolute uncertainty for a specific time, site and location can be calculated as follows:

1. Select the appropriate calibration factor from Table 6 for the period of interest.
2. Divide the reported PAN concentration by the calibration factor to obtain the peak height.
3. Read the corresponding relative uncertainty from Table B-3 and 4) multiply the relative uncertainty by the PAN concentration.

For example, to calculate the uncertainty in the 3 ppb PAN concentration reported for Burbank on August 27 at 8:01: (1) select the calibration factor of 0.595 from Table 6; (2)  $3 \div 0.595 = 5$  mm; (3) from Table B-3 the relative uncertainty is 0.23; and 4) the absolute uncertainty is  $\pm 0.7$  ppb. The actual uncertainties may vary slightly from those calculated by the above method since the relative uncertainties in Table B-3 are based upon generalizations about uncertainties in the instrument calibration factors.

At the Rubidoux site for the period 7/14 to 7/16 the correlation between peak height and calibration factor was 20% instead of 4.5%. Uncertainties thus calculated range from 58% at the lowest PAN levels to 30% at the highest values. For all other locations and periods calculated uncertainties range from ~51% at the lowest PAN levels to 12% at the highest values. Mid-range values are 13-19%.

## APPENDIX C

### DATA REPORT

## ORGANIZATION AND CONTENTS OF THE DATA REPORT

As part of the Southern California Air Quality Study (SCAQS), Daniel Grosjean and Associates, Inc. (DGA) carried out measurements of peroxyacetyl nitrate (PAN). Measurement methods, the corresponding analytical methods, calibration procedures, field operations, interlaboratory comparison studies and other technical aspects of our study are described in detail in the technical section of this report, which also includes a brief discussion of our findings. This data volume compiles all PAN data obtained by DGA during SCAQS.

Table C-1 presents PAN levels measured by DGA in samples collected on board the University of Washington, (UW) and Sonoma Technology, Inc. (STI) aircraft during selected SCAQS flights. PAN concentrations are reported in parts per billion (ppb) according to date, flight number, and sampling period.

Table C-2 is a compilation of ground-based measurements carried out at the SCAQS B sites as follows:

- Nine sites in June and July 1987: Anaheim, Azusa, Burbank, Claremont, Hawthorne, Long Beach, Los Angeles, Rubidoux, and San Nicholas Island.
- Seven sites in August and September 1987: Anaheim, Azusa, Burbank, Claremont, Long Beach, Los Angeles and Rubidoux.
- Five sites in November and December 1987: Anaheim, Burbank, Hawthorne, Long Beach and Los Angeles.

PAN concentrations are reported in ppb for each site (listed in alphabetical order) and each sampling event (listed in chronological order, PST). Uncertainties in individual data are not listed but can be readily calculated from page B-14 and Table B-3 of Appendix B, Error Analysis.

TABLE C-1. PAN AIRCRAFT DATA						
Date (1987)	Flight	DGA sample #	Sampling time, PST	PAN, µg/sample	V <sub>m</sub> (STP) (a)	PAN, ppb (STP)
6/19	UW1290	A013	15:21 - 15:53	6.0	0.81	1
		A014	16:15 - 16:46	≤2	0.82	0
		A015	17:08 - 17:37	≤2	0.76	0
		A016	17:56 - 18:31	≤2	0.91	0
6/24	UW1292	A017	4:50 - 5:20	13.0	0.74	3
		A018	5:38 - 6:13	24.0	0.89	5
		A019	6:36 - 7:11	15.3	0.90	3
		A020	7:25 - 7:55	29.0	0.78	7
6/25	UW1293	A021	4:54 - 5:26	21.8	0.80	5
		A022	5:41 - 6:13	10.1	0.82	2
		A023	7:02 - 7:27	11.5	0.64	3
		A024	7:41 - 8:10	24.2	0.75	6
	UW1294	A026	13:40 - 14:06	64.0	0.66	19
		A030	14:21 - 14:52	48.8	0.86	11
		A028	15:04 - 15:37	78.2	0.77	20
		A029	15:47 - 16:16	33.6	0.80	8
7/13	UW1302	A032	5:14 - 5:53	≤2	1.00	0
		A033	6:04 - 6:33	≤2	0.75	0
		A034	6:45 - 7:18	≤2	0.86	0
		A035	7:26 - 7:58	≤2	0.84	0
7/14	UW1304	A036	4:53 - 5:26	≤2	0.83	0
		A037	5:37 - 6:09	≤2	0.83	0
		A038	6:46 - 7:18	sample lost	0.83	no data
		A039	7:36 - 8:06	5.7	0.76	1
7/14	UW1305	A040	14:42 - 15:12	≤2	0.76	0
		A041	15:24 - 15:57	94.0	0.85	22
		A042	16:03 - 16:33	79.1	0.78	20
		A043	16:44 - 17:14	29.0	0.78	7
7/15	UW1306	A044	4:49 - 5:20	17.4	0.78	4
		A045	5:29 - 6:00	6.0	0.80	1
		A046	6:23 - 6:54	5.9	0.79	1
		A047	7:21 - 7:54	≤2	0.85	0
	UW1307	A049	15:00 - 15:30	39.6	0.76	10
		A050	15:43 - 16:14	93.0	0.80	23
		A005	16:20 - 16:50	59.1	0.77	15
		A006	16:58 - 17:30	67.7	0.83	16

Table C-1. PAN Aircraft Data (continued)						
Date (1987)	Flight	DGA sample #	Sampling time, PST	PAN, $\mu\text{g}/\text{sample}$	V, m (STP) (a)	PAN, ppb (STP)
8/27	STI66	A005(b)	5:58 - 6:25	32.7 (b)	0.403	6(b)
	STI69	A005(b)	15:38 - 16:08	32.7 (b)	0.633	6(b)
		A008	17:49 - 18:19	$\leq 2$	0.600	0
8/28	STI70	A012	5:51 - 6:23	25.5	0.528	9
		A011	7:43 - 8:15	$\leq 2$	0.552	0
9/2	STI71	A009	6:01 - 6:32	13.7	0.472	5
		A013	7:39 - 8:10	15.6	0.551	5
	STI73	A015	15:28 - 15:58	40.8	0.603	13
		A017	17:50 - 18:20	41.8	0.619	13
9/3	STI74	A014	5:44 - 6:16	19.0	0.492	7
		A018	7:25 - 7:56	27.1	0.565	9
11/12	STI76	A001	5:29 - 5:38	$\leq 2$	0.753	0
		A002	7:46 - 8:18	$\leq 2$	0.617	0
	STI77	A003	13:52 - 14:30	sample lost	0.642	no data
		A004	15:59 - 16:34	sample lost	0.712	no data
11/13	STI78	A005	5:41 - 6:28	11.7	0.493	4
		A006	7:35 - 8:07	26.6	0.623	8
	STI79	A007	13:51 - 14:26	60.8	0.700	17
		A008	15:46 - 16:21	107	0.684	31
11/14	STI80	A009	5:42 - 6:17	74.8	0.701	21
		A010	7:56 - 8:27	sample lost	0.737	no data
	STI81	A011	13:59 - 14:36	112	0.742	30
		A012	15:50 - 16:25	57.8	0.705	16
12/3	STI82	A013	5:14 - 6:16	21.6	0.565	7
		A014	7:37 - 8:08	$\leq 2$	0.578	0
	STI83	A015	13:33 - 14:08	61.5	0.708	17
		A016	15:38 - 16:13	95.3	0.699	27
12/10	STI84	A017	9:50 - 10:23	$\leq 2$	0.573	0
		A018	10:56 - 11:30	$\leq 2$	0.626	0
	STI85	A019	13:44 - 14:19	105.0	0.696	30
		A020	15:45 - 16:20	$\leq 2$	0.694	0
12/11	STI86	A021	5:35 - 6:09	72.0	0.643	22
		A022	7:21 - 7:55	14.8	-(c)	4 (c)
	STI87	A031	13:33 - 14:08	64.5	0.702	18
		A032	15:58 - 16:33	sample lost	0.695	no data
(a) as reported by UW and STI. STI also reported V (actual)						
(b) the same filter sample, A005, was used by mistake on two consecutive sampling periods.						
(c) not available, PAN estimated for a "typical" volume of 0.650 m						

TABLE C-1. (continued).				
Laboratory blanks and field controls (analytical detection limit = 1 µg per sample)				
Date (1987)	Flight	DGA sample #	PAN, µg/sample	
6/16	-	Laboratory blank	<1	
6/16	-	Laboratory blank	<1	
8/25	-	Laboratory blank	<1	
8/25	-	Laboratory blank	<1	
11/10	-	Laboratory blank	<1	
11/10	-	Laboratory blank	<1	
6/24	UW1292	A025	2	
6/25	1294	A031	1	
7/15	1306	A048	<1	
8/27	STI 66	A006	1	
	69	A007	<1	
9/2	71	A010	<1	
	73	A016	2	
9/3	74	A019	2	
11/12	76	A023	1	
	77	A024	<1	
11/13	78	A025	2	
	79	A026	2	
11/14	80	A027	1	
	81	A028	<1	
12/3	82	A030	<1	
	83	A029	<1	
12/14	84	A036	<1	
	85	A035	2	
12/11	86	A034	1	
	87	A033	<1	

**TABLE C-2**

**AMBIENT PAN AT SCAQS A AND B SITES**





	ANAHEIM PAN DATA	
Date	Time /PST	PAN /ppbv
6/18/87	23:56	<4
6/19/87	0:26	<8
6/19/87	0:56	<8
6/19/87	1:26	<4
6/19/87	1:56	<8
6/19/87	2:26	<8
6/19/87	2:56	<2
6/19/87	3:26	2
6/19/87	3:56	<3
6/19/87	4:26	<4
6/19/87	4:56	<4
6/19/87	5:26	<8
6/19/87	5:56	2
6/19/87	6:26	5
6/19/87	6:56	<6
6/19/87	7:26	<6
6/19/87	7:56	<6
6/19/87	8:26	<6
6/19/87	8:56	<3
6/19/87	9:26	<6
6/19/87	9:56	<6
6/19/87	10:26	<6
6/19/87	10:56	<6
6/19/87	11:26	<4
6/19/87	11:56	<8
6/19/87	12:26	<4
6/19/87	12:56	<4
6/19/87	13:26	<6
6/19/87	13:56	<4
6/19/87	14:26	<4
6/19/87	14:56	<6
6/19/87	15:26	<4
6/19/87	16:26	<4
6/19/87	16:56	<6
6/19/87	17:26	<6
6/19/87	17:56	<4
6/19/87	18:26	<6
6/19/87	18:56	<4
6/19/87	19:26	<4
6/19/87	19:56	<6

	ANAHEIM PAN DATA	
Date	Time /PST	PAN /ppbv
6/19/87	20:26	<4
6/19/87	20:56	5
6/19/87	21:26	<6
6/19/87	21:56	2
6/19/87	22:26	<6
6/19/87	22:56	<8
6/19/87	23:26	<4
6/19/87	23:56	<6
6/23/87	23:58	<6
6/24/87	0:28	5
6/24/87	0:58	6
6/24/87	1:28	6
6/24/87	1:58	4
6/24/87	2:28	5
6/24/87	2:58	<6
6/24/87	3:28	<6
6/24/87	3:58	5
6/24/87	4:28	2
6/24/87	4:58	7
6/24/87	5:28	<6
6/24/87	5:58	4
6/24/87	6:28	<6
6/24/87	6:58	7
6/24/87	7:28	2
6/24/87	7:58	<6
6/24/87	8:28	<6
6/24/87	8:58	<6
6/24/87	9:28	2
6/24/87	9:58	<8
6/24/87	10:28	<8
6/24/87	10:58	ND
6/24/87	11:28	ND
6/24/87	11:58	ND
6/24/87	12:28	ND
6/24/87	12:58	ND
6/24/87	13:28	<2
6/24/87	13:58	<2
6/24/87	14:28	<2
6/24/87	17:23	<6
6/24/87	18:23	4
6/24/87	19:23	<6
6/24/87	20:23	2

	ANAHEIM	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
6/24/87	21:23	<6
6/24/87	22:23	2
6/24/87	23:23	3
6/25/87	0:23	6
6/25/87	1:23	<6
6/25/87	2:23	1
6/25/87	3:23	<6
6/25/87	4:23	<6
6/25/87	5:23	2
6/25/87	6:23	<6
6/25/87	7:23	<2
6/25/87	8:23	<6
6/25/87	9:23	<2
6/25/87	10:23	6
6/25/87	11:24	<3
6/25/87	12:24	2
6/25/87	13:24	4
6/25/87	14:24	<2
6/25/87	15:24	<3
6/25/87	16:24	<2
6/25/87	17:24	<4
6/25/87	18:24	<2
6/25/87	19:24	<2
6/25/87	20:24	2
6/25/87	21:24	<4
6/25/87	22:24	<4
6/25/87	23:24	<6
6/26/87	0:24	<4
7/12/87	19:33	0.7
7/12/87	20:33	0.2
7/12/87	21:33	0.4
7/12/87	22:33	0.4
7/12/87	23:33	0.3
7/13/87	0:33	0.3
7/13/87	1:33	0.4
7/13/87	2:33	0.3
7/13/87	3:33	0.0
7/13/87	4:33	0.2
7/13/87	5:33	0.3
7/13/87	6:33	0.5
7/13/87	7:33	0.4
7/13/87	8:33	0.7

	ANAHEIM	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
7/13/87	9:33	1.5
7/13/87	10:33	0.9
7/13/87	11:36	0.4
7/13/87	12:39	1.9
7/13/87	13:26	2.3
7/13/87	14:26	2.0
7/13/87	15:26	1.6
7/13/87	16:26	1.8
7/13/87	17:26	1.5
7/13/87	18:26	0.5
7/13/87	19:26	0.4
7/13/87	20:26	0.4
7/13/87	21:26	0.5
7/13/87	22:26	0.3
7/13/87	23:26	0.2
7/14/87	0:26	0.2
7/14/87	1:26	0.4
7/14/87	2:26	0.1
7/14/87	3:26	0.1
7/14/87	4:26	0.2
7/14/87	5:26	0.2
7/14/87	6:26	0.3
7/14/87	7:26	0.4
7/14/87	8:26	0.8
7/14/87	9:26	0.7
7/14/87	10:26	1.0
7/14/87	11:26	1.4
7/14/87	12:26	1.2
7/14/87	13:26	1.4
7/14/87	12:26	2.2
7/14/87	15:26	2.4
7/14/87	16:26	1.3
7/14/87	17:27	1.9
7/14/87	18:27	0.2
7/14/87	19:27	0.3
7/14/87	20:27	0.4
7/14/87	21:27	0.4
7/14/87	22:27	ND
7/14/87	23:27	ND
7/15/87	0:33	0.2
7/15/87	1:33	0.3
7/15/87	2:33	0.2

	ANAHEIM	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
7/15/87	3:33	0.5
7/15/87	4:33	0.3
7/15/87	5:33	0.6
7/15/87	6:33	0.5
7/15/87	7:33	0.2
7/15/87	8:33	0.7
7/15/87	9:33	0.5
7/15/87	10:33	0.1
7/15/87	11:33	0.3
7/15/87	12:33	0.9
7/15/87	13:33	0.5
7/15/87	14:33	0.6
7/15/87	15:33	1.0
7/15/87	16:33	1.3
7/15/87	17:33	0.2
7/15/87	18:33	0.3
7/15/87	19:33	0.5
7/15/87	20:33	0.1
7/15/87	21:33	0.1
7/15/87	22:33	ND
8/26/87	20:06	0.0
8/26/87	21:06	0.0
8/26/87	22:06	0.0
8/26/87	23:06	0.0
8/27/87	0:06	0.0
8/27/87	1:06	0.0
8/27/87	2:06	0.0
8/27/87	3:06	0.2
8/27/87	4:06	0.0
8/27/87	5:06	0.0
8/27/87	6:06	0.0
8/27/87	7:06	0.0
8/27/87	8:06	0.0
8/27/87	9:06	0.0
8/27/87	10:06	0.2
8/27/87	11:06	1.1
8/27/87	12:06	1.1
8/27/87	13:06	0.4
8/27/87	14:06	0.4
8/27/87	15:06	0.4
8/27/87	16:06	0.9
8/27/87	17:06	0.2

	ANAHEIM	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
8/27/87	18:06	0.0
8/27/87	19:06	0.2
8/27/87	20:06	0.0
8/27/87	21:06	0.0
8/27/87	22:06	0.0
8/27/87	23:06	0.0
8/28/87	0:07	0.2
8/28/87	1:07	0.0
8/28/87	2:07	0.0
8/28/87	3:07	0.0
8/28/87	4:07	0.2
8/28/87	5:07	0.0
8/28/87	6:07	0.0
8/28/87	7:07	0.0
8/28/87	8:07	0.0
8/28/87	9:07	0.0
8/28/87	10:07	0.2
8/28/87	11:07	0.2
8/28/87	12:07	1.1
8/28/87	13:07	0.9
8/28/87	14:07	0.9
8/28/87	15:07	0.9
8/28/87	16:07	1.0
8/28/87	17:07	0.9
8/28/87	18:07	0.0
8/28/87	19:07	0.0
8/28/87	20:07	0.0
8/28/87	21:07	0.0
8/28/87	22:07	0.2
8/28/87	23:07	0.0
8/29/87	0:07	0.0
8/29/87	1:07	0.0
8/29/87	2:07	0.2
8/29/87	3:07	0.0
8/29/87	4:07	0.0
8/29/87	5:07	0.0
8/29/87	6:07	0.0
8/29/87	7:07	0.4
8/29/87	8:07	0.0
8/29/87	9:07	0.0
8/29/87	10:07	0.0
8/29/87	11:07	0.0

	ANAHEIM	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
8/29/87	12:07	0.0
8/29/87	13:07	0.0
8/29/87	14:07	0.0
8/29/87	15:07	0.2
8/29/87	16:07	0.2
8/29/87	17:07	0.0
8/29/87	18:07	0.0
8/29/87	19:07	0.0
8/29/87	20:07	0.0
8/29/87	21:07	0.0
8/29/87	22:07	0.0
8/29/87	23:07	0.0
8/30/87	0:07	0.0
9/1/87	20:41	0.0
9/1/87	21:41	0.0
9/1/87	22:41	0.0
9/1/87	23:41	0.0
9/2/87	0:41	0.0
9/2/87	1:41	0.0
9/2/87	2:41	0.0
9/2/87	3:41	0.0
9/2/87	4:41	0.0
9/2/87	5:41	0.0
9/2/87	6:41	0.0
9/2/87	7:41	0.0
9/2/87	8:41	0.0
9/2/87	9:41	0.2
9/2/87	11:10	1.1
9/2/87	12:10	1.1
9/2/87	13:02	0.4
9/2/87	14:02	0.9
9/2/87	15:02	1.3
9/2/87	16:02	1.1
9/2/87	17:02	0.2
9/2/87	18:02	0.0
9/2/87	19:02	0.0
9/2/87	20:02	0.0
9/2/87	21:02	0.0
9/2/87	22:02	0.0
9/2/87	23:02	0.0
9/3/87	0:02	0.0
9/3/87	1:02	0.0

	ANAHEIM	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
9/3/87	2:02	0.0
9/3/87	3:02	0.0
9/3/87	4:02	0.0
9/3/87	5:02	0.0
9/3/87	6:02	0.0
9/3/87	7:02	0.0
9/3/87	8:02	0.0
9/3/87	9:02	0.0
9/3/87	10:02	1.1
9/3/87	11:02	1.1
9/3/87	12:02	0.4
9/3/87	13:02	0.0
9/3/87	14:02	0.0
9/3/87	15:03	0.0
9/3/87	16:03	0.0
9/3/87	17:03	0.0
9/3/87	18:03	0.0
9/3/87	19:03	0.0
9/3/87	20:03	0.2
9/3/87	21:03	0.0
9/3/87	22:03	0.0
9/3/87	23:03	0.0
11/11/87	0:39	0.0
11/11/87	1:39	0.0
11/11/87	2:39	0.4
11/11/87	3:39	0.0
11/11/87	4:39	0.0
11/11/87	5:39	0.0
11/11/87	6:39	0.0
11/11/87	7:39	0.5
11/11/87	8:39	0.0
11/11/87	9:39	0.5
11/11/87	10:39	0.5
11/11/87	11:39	0.0
11/11/87	12:39	0.0
11/11/87	13:39	1.8
11/11/87	14:39	3.1
11/11/87	15:39	2.2
11/11/87	16:39	2.7
11/11/87	17:39	3.1
11/11/87	18:39	2.7
11/11/87	19:39	2.2

	ANAHEIM	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
11/11/87	20:39	1.3
11/11/87	21:39	1.8
11/11/87	22:39	0.9
11/11/87	23:39	0.9
11/12/87	0:39	0.0
11/12/87	1:39	1.3
11/12/87	2:39	1.8
11/12/87	3:39	1.3
11/12/87	4:39	0.9
11/12/87	5:39	0.4
11/12/87	6:39	0.4
11/12/87	7:39	0.9
11/12/87	8:39	0.9
11/12/87	9:39	1.8
11/12/87	10:39	4.0
11/12/87	11:39	6.7
11/12/87	12:39	6.2
11/12/87	13:39	5.3
11/12/87	14:39	3.6
11/12/87	15:48	2.2
11/12/87	16:34	4.0
11/12/87	17:34	3.6
11/12/87	18:34	4.9
11/12/87	19:34	1.8
11/12/87	20:34	1.3
11/12/87	21:34	1.3
11/12/87	22:34	1.8
11/12/87	23:34	2.2
11/13/87	0:34	1.3
11/13/87	1:34	2.2
11/13/87	2:34	1.8
11/13/87	3:34	2.2
11/13/87	4:34	2.2
11/13/87	5:34	2.2
11/13/87	6:34	2.2
11/13/87	7:34	2.2
11/13/87	8:34	1.8
11/13/87	9:34	3.1
11/13/87	10:34	4.0
11/13/87	11:34	0.0
11/13/87	12:34	3.1
11/13/87	13:34	1.8

	ANAHEIM	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
11/13/87	14:34	1.3
11/13/87	15:34	1.3
11/13/87	16:34	1.8
11/13/87	17:34	0.9
11/13/87	18:34	0.9
11/13/87	19:34	1.3
11/13/87	20:34	0.9
11/13/87	21:34	0.0
11/13/87	22:34	0.9
11/13/87	23:34	0.0
11/14/87	0:34	0.0
12/3/87	0:10	4.9
12/3/87	1:10	4.9
12/3/87	2:10	6.2
12/3/87	3:10	6.2
12/3/87	4:10	7.6
12/3/87	5:10	5.8
12/3/87	6:10	4.9
12/3/87	7:10	4.0
12/3/87	8:10	3.6
12/3/87	9:10	4.9
12/3/87	10:10	8.9
12/3/87	11:10	11.6
12/3/87	12:10	13.4
12/3/87	13:10	16.0
12/3/87	14:10	14.2
12/3/87	15:10	18.7
12/3/87	16:10	16.5
12/3/87	17:10	12.0
12/3/87	18:10	10.2
12/3/87	19:10	8.9
12/3/87	20:10	7.1
12/3/87	21:10	6.7
12/3/87	22:10	4.5
12/3/87	23:10	9.3
12/10/87	0:33	1.8
12/10/87	1:33	1.8
12/10/87	2:33	0.9
12/10/87	3:33	0.0
12/10/87	4:33	0.0
12/10/87	5:33	0.0
12/10/87	6:33	1.3

	ANAHEIM	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
12/10/87	7:33	1.8
12/10/87	8:33	1.3
12/10/87	9:33	2.7
12/10/87	10:33	1.3
12/10/87	11:33	2.2
12/10/87	12:33	2.7
12/10/87	13:33	4.9
12/10/87	14:33	8.5
12/10/87	15:33	5.8
12/10/87	16:33	7.1
12/10/87	17:33	6.7
12/10/87	18:33	4.5
12/10/87	19:33	3.1
12/10/87	20:33	4.0
12/10/87	21:33	2.7
12/10/87	22:33	2.2
12/10/87	23:33	1.3
12/11/87	0:33	1.3
12/11/87	1:33	1.3
12/11/87	2:33	1.3
12/11/87	3:33	1.3
12/11/87	4:33	1.3
12/11/87	5:33	1.3
12/11/87	6:33	1.3
12/11/87	7:33	1.3
12/11/87	8:33	1.8
12/11/87	9:34	2.2
12/11/87	10:34	3.6
12/11/87	11:34	5.8
12/11/87	12:34	8.0
12/11/87	13:34	7.6
12/11/87	14:34	7.6
12/11/87	15:34	7.6
12/11/87	16:34	6.7
12/11/87	17:34	8.0
12/11/87	18:34	4.9
12/11/87	19:34	3.6
12/11/87	20:34	3.1
12/11/87	21:34	3.1
12/11/87	22:34	2.2
12/11/87	23:34	2.2

	AZUSA	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
6/18/87	23:12	1
6/18/87	23:42	2
6/19/87	0:12	1
6/19/87	0:42	2
6/19/87	1:12	2
6/19/87	1:42	0
6/19/87	2:12	3
6/19/87	2:42	2
6/19/87	3:12	2
6/19/87	3:42	1
6/19/87	4:12	2
6/19/87	4:42	2
6/19/87	5:12	2
6/19/87	5:42	2
6/19/87	6:12	0
6/19/87	6:42	2
6/19/87	7:12	2
6/19/87	7:42	0
6/19/87	8:12	2
6/19/87	8:42	3
6/19/87	9:12	4
6/19/87	9:42	4
6/19/87	10:12	4
6/19/87	10:42	6
6/19/87	11:12	6
6/19/87	11:42	6
6/19/87	12:12	4
6/19/87	13:34	6
6/19/87	14:04	6
6/19/87	14:34	6
6/19/87	15:04	6
6/19/87	15:34	4
6/19/87	16:04	5
6/19/87	16:34	5
6/19/87	17:04	5
6/19/87	17:34	5
6/19/87	18:04	4
6/19/87	18:34	4
6/19/87	19:04	3
6/19/87	19:34	3
6/19/87	20:04	2
6/19/87	20:34	2

	AZUSA	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
6/19/87	21:04	2
6/19/87	21:34	2
6/19/87	22:04	1
6/19/87	22:34	2
6/19/87	23:04	1
6/19/87	23:34	3
6/20/87	0:04	1
6/20/87	0:34	2
6/23/87	20:45	3
6/23/87	21:14	1
6/23/87	21:45	1
6/23/87	22:14	2
6/23/87	22:45	2
6/23/87	23:14	2
6/23/87	23:45	0
6/24/87	0:14	0
6/24/87	0:45	2
6/24/87	1:14	2
6/24/87	1:45	1
6/24/87	2:14	2
6/24/87	2:45	2
6/24/87	3:14	2
6/24/87	3:45	2
6/24/87	4:14	2
6/24/87	4:45	2
6/24/87	5:14	3
6/24/87	5:45	6
6/24/87	6:14	6
6/24/87	6:45	3
6/24/87	7:14	3
6/24/87	7:45	3
6/24/87	8:14	4
6/24/87	8:45	4
6/24/87	9:14	5
6/24/87	9:45	5
6/24/87	10:14	6
6/24/87	10:45	8
6/24/87	11:14	9
6/24/87	11:45	10
6/24/87	12:14	11
6/24/87	12:45	10
6/24/87	13:14	11
6/24/87	13:45	12



	AZUSA	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
6/24/87	14:14	12
6/24/87	14:45	10
6/24/87	15:14	10
6/24/87	15:45	9
6/24/87	16:14	8
6/24/87	16:45	8
6/24/87	17:14	6
6/24/87	17:45	5
6/24/87	18:14	5
6/24/87	18:45	3
6/24/87	19:14	2
6/24/87	19:45	2
6/24/87	20:14	2
6/24/87	20:45	2
6/24/87	21:15	2
6/24/87	21:45	1
6/24/87	22:15	2
6/24/87	22:45	2
6/24/87	23:15	2
6/24/87	23:45	2
6/25/87	0:15	1
6/25/87	0:45	2
6/25/87	1:15	2
6/25/87	1:45	3
6/25/87	2:15	2
6/25/87	2:45	1
6/25/87	3:15	1
6/25/87	3:45	2
6/25/87	4:15	2
6/25/87	4:45	2
6/25/87	5:15	3
6/25/87	5:45	2
6/25/87	6:15	2
6/25/87	6:45	3
6/25/87	7:15	3
6/25/87	7:45	3
6/25/87	8:15	2
6/25/87	8:45	3
6/25/87	9:15	4
6/25/87	9:45	6
6/25/87	10:15	8
6/25/87	10:45	9
6/25/87	11:15	10

	AZUSA	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
6/25/87	11:45	11
6/25/87	12:15	11
6/25/87	12:45	9
6/25/87	2:36	6
6/25/87	13:45	7
6/25/87	14:15	7
6/25/87	14:45	7
6/25/87	15:15	6
6/25/87	15:45	5
6/25/87	16:15	6
6/25/87	16:45	5
6/25/87	17:15	6
6/25/87	17:45	6
6/25/87	18:15	5
6/25/87	18:45	5
6/25/87	19:15	4
6/25/87	19:45	2
6/25/87	20:15	3
6/25/87	20:45	2
6/25/87	21:15	3
6/25/87	21:45	3
6/25/87	22:15	2
6/25/87	22:45	3
6/25/87	23:15	3
6/25/87	23:45	2
6/26/87	0:15	2
6/26/87	0:45	2
6/26/87	1:15	3
7/12/87	20:18	2
7/12/87	20:48	1
7/12/87	21:18	0
7/12/87	21:48	0
7/12/87	22:18	1
7/12/87	22:48	2
7/12/87	23:18	0
7/12/87	23:48	0
7/13/87	0:18	0
7/13/87	0:48	ND
7/13/87	12:16	8
7/13/87	12:47	10
7/13/87	13:16	9
7/13/87	13:47	6
7/13/87	14:16	6

	AZUSA	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
7/13/87	14:47	5
7/13/87	15:16	3
7/13/87	15:47	2
7/13/87	16:16	2
7/13/87	16:47	3
7/13/87	17:16	2
7/13/87	17:47	2
7/13/87	18:17	2
7/13/87	18:47	2
7/13/87	19:17	2
7/13/87	19:47	2
7/13/87	20:17	2
7/13/87	20:47	2
7/13/87	21:17	2
7/13/87	21:47	2
7/13/87	22:17	2
7/13/87	22:47	2
7/13/87	23:17	0
7/13/87	23:47	0
7/14/87	0:17	0
7/14/87	0:47	0
7/14/87	1:17	0
7/14/87	1:47	2
7/14/87	2:17	0
7/14/87	2:47	0
7/14/87	3:17	1
7/14/87	3:47	1
7/14/87	4:17	1
7/14/87	4:47	1
7/14/87	5:17	1
7/14/87	5:47	1
7/14/87	6:17	2
7/14/87	6:47	0
7/14/87	7:17	0
7/14/87	7:47	1
7/14/87	8:17	1
7/14/87	8:47	2
7/14/87	9:17	2
7/14/87	9:47	3
7/14/87	10:17	3
7/14/87	10:47	3
7/14/87	11:17	4
7/14/87	17:47	0

	AZUSA	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
7/14/87	18:17	2
7/14/87	18:47	2
7/14/87	19:17	2
7/14/87	19:47	2
7/14/87	20:17	2
7/14/87	20:47	2
7/14/87	21:17	2
7/14/87	21:47	2
7/14/87	22:17	2
7/14/87	22:47	2
7/14/87	23:17	2
7/14/87	23:47	2
7/15/87	0:17	2
7/15/87	0:47	2
7/15/87	1:17	2
7/15/87	1:47	2
7/15/87	2:17	2
7/15/87	2:48	2
7/15/87	3:17	2
7/15/87	3:48	2
7/15/87	4:17	2
7/15/87	4:48	2
7/15/87	5:17	2
7/15/87	5:48	2
7/15/87	6:17	2
7/15/87	6:48	2
7/15/87	7:17	3
7/15/87	7:48	2
7/15/87	8:17	2
7/15/87	8:48	3
7/15/87	9:17	3
7/15/87	9:48	4
7/15/87	10:17	3
7/15/87	10:48	3
7/15/87	11:17	3
7/15/87	11:48	4
7/15/87	12:17	5
7/15/87	12:48	6
7/15/87	13:17	6
7/15/87	13:48	7
7/15/87	14:17	6
7/15/87	14:48	6
7/15/87	15:17	5

	AZUSA	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
7/15/87	15:48	5
7/15/87	16:17	6
7/15/87	16:48	6
7/15/87	17:17	5
7/15/87	17:48	5
7/15/87	18:17	4
7/15/87	18:48	4
7/15/87	19:17	3
7/15/87	19:48	3
7/15/87	20:17	3
7/15/87	20:48	3
7/15/87	21:17	4
7/15/87	21:48	3
7/15/87	22:17	2
7/15/87	22:48	2
7/15/87	23:17	3
7/15/87	23:48	2
7/16/87	0:17	3
7/16/87	0:48	2
8/27/87	0:04	0
8/27/87	0:35	1
8/27/87	1:04	0
8/27/87	1:35	0
8/27/87	2:04	0
8/27/87	2:35	0
8/27/87	3:04	0
8/27/87	3:35	0
8/27/87	4:04	0
8/27/87	4:35	0
8/27/87	5:05	0
8/27/87	5:35	0
8/27/87	6:05	0
8/27/87	6:35	0
8/27/87	7:05	2
8/27/87	7:35	3
8/27/87	8:05	2
8/27/87	8:35	3
8/27/87	9:05	4
8/27/87	9:35	4
8/27/87	10:05	4
8/27/87	10:35	5
8/27/87	11:05	6
8/27/87	11:35	7

	AZUSA	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
8/27/87	12:05	8
8/27/87	12:35	9
8/27/87	13:05	9
8/27/87	13:35	8
8/27/87	14:05	6
8/27/87	14:35	6
8/27/87	15:05	6
8/27/87	15:35	6
8/27/87	16:05	5
8/27/87	16:35	4
8/27/87	17:05	3
8/27/87	17:35	2
8/27/87	18:05	2
8/27/87	18:35	2
8/27/87	19:05	2
8/27/87	19:35	0
8/27/87	20:05	2
8/27/87	20:35	2
8/27/87	21:05	0
8/27/87	21:35	2
8/27/87	22:05	0
8/27/87	22:35	0
8/27/87	23:05	0
8/27/87	23:35	2
8/28/87	0:05	0
8/28/87	0:35	0
8/28/87	1:05	0
8/28/87	1:35	0
8/28/87	2:05	0
8/28/87	2:35	0
8/28/87	3:05	0
8/28/87	3:35	0
8/28/87	4:05	0
8/28/87	4:35	0
8/28/87	5:05	2
8/28/87	5:35	0
8/28/87	6:05	0
8/28/87	6:35	0
8/28/87	7:05	0
8/28/87	7:35	2
8/28/87	8:05	2
8/28/87	8:35	2
8/28/87	9:05	3

	AZUSA	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
8/28/87	9:35	3
8/28/87	10:05	3
8/28/87	10:35	5
8/28/87	11:05	6
8/28/87	11:35	8
8/28/87	12:05	7
8/28/87	12:35	11
8/28/87	13:05	11
8/28/87	13:35	12
8/28/87	14:05	13
8/28/87	14:35	10
8/28/87	15:05	8
8/28/87	15:35	8
8/28/87	16:05	7
8/28/87	16:35	6
8/28/87	17:05	4
8/28/87	17:35	4
8/28/87	18:05	3
8/28/87	18:35	3
8/28/87	19:05	2
8/28/87	19:35	2
8/28/87	20:05	0
8/28/87	20:35	2
8/28/87	21:05	2
8/28/87	21:35	0
8/28/87	22:05	2
8/28/87	22:35	2
8/28/87	23:05	2
8/28/87	23:35	0
8/29/87	0:05	0
8/29/87	0:35	0
8/29/87	1:05	0
8/29/87	1:35	0
8/29/87	2:05	0
8/29/87	2:35	0
8/29/87	3:05	0
8/29/87	3:35	2
8/29/87	4:05	0
8/29/87	4:35	0
8/29/87	5:05	0
8/29/87	5:35	0
8/29/87	6:05	0
8/29/87	6:35	2

	AZUSA	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
8/29/87	7:05	0
8/29/87	7:35	2
8/29/87	8:05	0
8/29/87	8:35	2
8/29/87	9:05	2
8/29/87	9:35	3
8/29/87	10:05	4
8/29/87	10:35	4
8/29/87	11:05	6
8/29/87	11:35	7
8/29/87	12:05	8
8/29/87	12:35	11
8/29/87	13:05	12
8/29/87	13:35	13
8/29/87	14:05	12
8/29/87	15:05	12
8/29/87	15:35	11
8/29/87	16:05	11
8/29/87	16:35	11
8/29/87	17:05	8
8/29/87	17:35	8
8/29/87	18:05	7
8/29/87	18:35	6
8/29/87	19:05	6
8/29/87	19:35	4
8/29/87	20:05	2
8/29/87	20:35	2
8/29/87	21:05	3
8/29/87	21:35	2
8/29/87	22:05	2
8/29/87	22:35	2
8/29/87	23:05	2
8/29/87	23:35	0
8/30/87	0:05	0
9/1/87	23:06	0
9/1/87	23:36	0
9/2/87	0:06	0
9/2/87	0:36	0
9/2/87	1:06	0
9/2/87	1:36	0
9/2/87	2:06	0
9/2/87	2:36	0
9/2/87	3:06	0

	AZUSA	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
9/2/87	3:37	0
9/2/87	4:06	0
9/2/87	4:37	0
9/2/87	5:07	0
9/2/87	5:37	0
9/2/87	6:07	0
9/2/87	6:37	2
9/2/87	7:07	2
9/2/87	7:37	2
9/2/87	8:07	0
9/2/87	8:37	2
9/2/87	9:07	0
9/2/87	9:37	2
9/2/87	10:07	2
9/2/87	10:37	2
9/2/87	11:07	0
9/2/87	11:37	2
9/2/87	12:07	0
9/2/87	7:52	0
9/2/87	13:07	3
9/2/87	13:37	9
9/2/87	14:07	9
9/2/87	14:37	8
9/2/87	15:07	9
9/2/87	15:37	6
9/2/87	16:07	4
9/2/87	16:37	4
9/2/87	17:07	4
9/2/87	17:37	3
9/2/87	18:07	3
9/2/87	18:37	3
9/2/87	19:07	3
9/2/87	19:37	2
9/2/87	20:07	2
9/2/87	20:37	2
9/2/87	21:07	0
9/2/87	21:37	0
9/2/87	22:07	0
9/2/87	22:37	2
9/2/87	23:07	0
9/2/87	23:37	0
9/3/87	0:07	2
9/3/87	0:37	0

	AZUSA	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
9/3/87	1:07	0
9/3/87	1:37	0
9/3/87	2:07	0
9/3/87	2:37	0
9/3/87	3:07	0
9/3/87	3:37	0
9/3/87	4:07	0
9/3/87	4:37	0
9/3/87	5:07	0
9/3/87	5:37	0
9/3/87	6:07	0
9/3/87	6:37	0
9/3/87	7:07	0
9/3/87	7:37	0
9/3/87	8:07	3
9/3/87	8:37	2
9/3/87	9:07	2
9/3/87	9:37	3
9/3/87	10:07	4
9/3/87	10:37	4
9/3/87	11:07	5
9/3/87	11:37	5
9/3/87	12:07	5
9/3/87	12:37	6
9/3/87	13:07	5
9/3/87	13:37	4
9/3/87	14:07	3
9/3/87	14:37	2
9/3/87	15:07	2
9/3/87	15:37	2
9/3/87	16:07	2
9/3/87	17:07	0
9/3/87	17:37	2
9/3/87	18:07	0
9/3/87	18:37	2
9/3/87	19:07	0
9/3/87	19:37	2
9/3/87	20:07	0

	BURBANK	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
6/19/87		ND
6/23/87	23:19	≤8
6/24/87	0:19	≤8
6/24/87	1:19	≤8
6/24/87	2:19	≤8
6/24/87	3:19	≤8
6/24/87	4:00	≤8
6/24/87	6:00	≤8
6/24/87	7:19	≤4
6/24/87	8:19	2
6/24/87	9:19	1
6/24/87	10:19	0
6/24/87	11:19	0
6/24/87	12:19	5
6/24/87	13:19	6
6/24/87	16:17	4
6/24/87	17:17	3
6/24/87	18:17	0
6/24/87	19:17	≤8
6/24/87	20:17	≤4
6/24/87	21:17	≤4
6/24/87	22:17	≤8
6/24/87	23:17	≤8
6/25/87	0:17	≤8
6/25/87	1:17	≤8
6/25/87	2:17	≤8
6/25/87	3:17	1
6/25/87	4:17	≤8
6/25/87	5:17	≤4
6/25/87	6:17	0
6/25/87	7:17	0
6/25/87	8:17	≤4
6/25/87	9:17	≤4
6/25/87	10:17	4
6/25/87	11:17	4
6/25/87	12:17	5
6/25/87	13:17	5
6/25/87	14:17	5
6/25/87	15:17	2
6/25/87	16:17	3
6/25/87	17:17	≤4
6/25/87	18:17	3

	BURBANK	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
6/25/87	19:17	≤4
6/25/87	20:16	≤4
6/25/87	21:16	≤8
6/25/87	22:16	≤8
6/25/87	23:16	≤8
6/26/87	0:16	≤8
7/12/87	21:40	1
7/12/87	22:40	0
7/12/87	23:40	0
7/13/87	0:40	0
7/13/87	1:40	0
7/13/87	2:40	0
7/13/87	3:40	0
7/13/87	4:40	0
7/13/87	5:40	0
7/13/87	6:40	0
7/13/87	7:40	0
7/13/87	8:40	0
7/13/87	9:36	2
7/13/87	10:36	3
7/13/87	11:36	3
7/13/87	12:36	4
7/13/87	13:36	4
7/13/87	14:36	3
7/13/87	15:36	2
7/13/87	16:36	2
7/13/87	17:36	0
7/13/87	18:36	0
7/13/87	19:30	0
7/13/87	20:36	0
7/13/87	21:36	0
7/13/87	22:36	0
7/13/87	23:36	0
7/14/87	0:36	0
7/14/87	1:36	0
7/14/87	2:36	0
7/14/87	3:36	0
7/14/87	4:36	0
7/14/87	5:36	0
7/14/87	6:36	0
7/14/87	7:36	0
7/14/87	8:36	0
7/14/87	9:36	2

	BURBANK	
	PAN DATA	
Date	Time /PST	PAN /ppbv
7/14/87	11:39	4
7/14/87	13:01	5
7/14/87	14:01	7
7/14/87	15:01	5
7/14/87	16:01	3
7/14/87	17:01	2
7/14/87	18:01	1
7/14/87	19:01	0
7/14/87	20:01	0
7/14/87	21:01	0
7/14/87	22:01	0
7/14/87	23:01	0
7/15/87	0:01	0
7/15/87	1:01	0
7/15/87	2:01	0
7/15/87	3:01	0
7/15/87	4:01	0
7/15/87	5:01	0
7/15/87	6:01	0
7/15/87	7:01	0
7/15/87	8:01	0
7/15/87	9:01	2
7/15/87	10:01	2
7/15/87	11:01	1
7/15/87	12:01	2
7/15/87	13:01	5
7/15/87	14:01	5
7/15/87	15:01	4
7/15/87	16:01	2
7/15/87	17:01	3
7/15/87	18:01	2
7/15/87	19:01	2
7/15/87	20:01	1
7/15/87	21:01	1
7/15/87	22:01	1
7/15/87	23:01	2
7/16/87	0:01	2
8/26/87	23:38	0
8/27/87	0:01	0
8/27/87	1:01	2
8/27/87	2:01	0
8/27/87	3:01	0
8/27/87	4:01	0

	BURBANK	
	PAN DATA	
Date	Time /PST	PAN /ppbv
8/27/87	5:01	0
8/27/87	6:01	0
8/27/87	7:01	0
8/27/87	8:01	3
8/27/87	9:01	4
8/27/87	10:01	6
8/27/87	11:01	8
8/27/87	12:01	10
8/27/87	13:01	9
8/27/87	14:01	8
8/27/87	15:01	6
8/27/87	16:01	3
8/27/87	17:01	3
8/27/87	18:01	2
8/27/87	19:01	2
8/27/87	20:01	0
8/27/87	21:01	0
8/27/87	22:01	0
8/27/87	23:01	0
8/28/87	0:01	0
8/28/87	1:01	0
8/28/87	2:01	0
8/28/87	3:01	0
8/28/87	4:01	0
8/28/87	5:01	0
8/28/87	6:01	0
8/28/87	7:01	0
8/28/87	8:01	2
8/28/87	9:01	3
8/28/87	10:01	6
8/28/87	11:01	9
8/28/87	12:01	11
8/28/87	13:01	12
8/28/87	14:01	11
8/28/87	15:01	8
8/28/87	16:01	4
8/28/87	17:01	4
8/28/87	18:01	2
8/28/87	19:01	2
8/28/87	21:01	2
8/28/87	22:02	1
8/28/87	23:02	2
8/29/87	0:02	0

	BURBANK	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
9/2/87	19:38	2
9/2/87	20:38	2
9/2/87	21:38	0
9/2/87	22:38	0
9/2/87	23:38	0
9/3/87	0:38	0
9/3/87	1:38	0
9/3/87	2:38	0
9/3/87	3:38	0
9/3/87	4:38	0
9/3/87	5:38	0
9/3/87	6:38	0
9/3/87	7:38	3
9/3/87	8:38	3
9/3/87	9:38	5
9/3/87	10:38	7
9/3/87	11:38	5
9/3/87	12:38	9
9/3/87	13:38	8
9/3/87	14:38	5
9/3/87	15:38	5
9/3/87	16:38	4
9/3/87	17:38	4
9/3/87	18:38	3
9/3/87	19:38	3
9/3/87	20:38	2
9/3/87	21:38	0
9/3/87	22:38	0
11/10/87	23:31	1
11/11/87	0:31	0
11/11/87	1:31	1
11/11/87	2:31	0
11/11/87	3:31	0
11/11/87	4:31	0
11/11/87	5:31	0
11/11/87	6:31	0
11/11/87	7:31	1
11/11/87	8:31	1
11/11/87	9:31	2
11/11/87	10:31	5
11/11/87	11:31	5
11/11/87	12:31	3
11/11/87	13:31	2

	BURBANK	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
8/29/87	1:02	0
8/29/87	2:02	2
8/29/87	3:02	0
8/29/87	4:02	0
8/29/87	5:02	0
8/29/87	6:02	0
8/29/87	7:02	0
8/29/87	8:02	2
8/29/87	9:02	4
8/29/87	10:02	4
8/29/87	11:02	8
8/29/87	12:02	11
8/29/87	13:02	13
8/29/87	14:02	13
8/29/87	15:02	12
8/29/87	16:02	13
8/29/87	17:02	9
8/29/87	18:02	5
8/29/87	19:02	5
8/29/87	20:02	4
8/29/87	21:02	2
8/29/87	22:02	3
8/29/87	23:02	1
8/30/87	0:02	2
9/2/87	0:38	0
9/2/87	1:38	0
9/2/87	2:38	0
9/2/87	3:38	0
9/2/87	4:38	0
9/2/87	5:38	0
9/2/87	6:38	0
9/2/87	7:38	0
9/2/87	8:38	0
9/2/87	9:38	2
9/2/87	10:38	2
9/2/87	11:38	7
9/2/87	12:38	8
9/2/87	13:38	10
9/2/87	14:38	7
9/2/87	15:38	5
9/2/87	16:38	3
9/2/87	17:38	3
9/2/87	18:38	3



	BURBANK	
	PAN DATA	
Date	Time /PST	PAN /ppbv
11/11/87	14:27	2
11/11/87	15:21	2
11/11/87	16:17	2
11/11/87	17:17	2
11/11/87	18:17	2
11/11/87	19:17	1
11/11/87	20:17	0
11/11/87	21:18	1
11/11/87	22:18	1
11/11/87	23:18	0
11/12/87	0:18	0
11/12/87	1:18	0
11/12/87	2:18	0
11/12/87	3:18	1
11/12/87	4:18	0
11/12/87	5:18	1
11/12/87	6:18	1
11/12/87	7:18	1
11/12/87	8:18	1
11/12/87	9:18	2
11/12/87	10:18	4
11/12/87	11:18	4
11/12/87	12:18	5
11/12/87	13:18	7
11/12/87	14:18	17
11/12/87	15:18	16
11/12/87	16:18	14
11/12/87	17:18	10
11/12/87	18:18	7
11/12/87	19:18	5
11/12/87	20:18	3
11/12/87	21:18	2
11/12/87	22:18	2
11/12/87	23:18	2
11/13/87	0:18	3
11/13/87	1:18	2
11/13/87	2:18	ND
11/13/87	3:18	2
11/13/87	4:18	6
11/13/87	5:18	2
11/13/87	6:18	2
11/13/87	7:18	3
11/13/87	8:18	2

	BURBANK	
	PAN DATA	
Date	Time /PST	PAN /ppbv
11/13/87	9:18	5
11/13/87	10:18	4
11/13/87	11:18	5
11/13/87	12:18	8
11/13/87	13:18	10
11/13/87	14:18	12
11/13/87	15:18	10
11/13/87	16:18	6
11/13/87	17:18	5
11/13/87	18:18	4
11/13/87	19:18	1
11/13/87	20:18	2
11/13/87	21:18	ND
11/13/87	22:18	2
11/13/87	23:18	0
11/14/87	0:18	2
12/3/87	0:29	5
12/3/87	1:29	3
12/3/87	2:29	4
12/3/87	3:29	3
12/3/87	4:29	3
12/3/87	5:29	3
12/3/87	6:29	3
12/3/87	7:29	4
12/3/87	8:29	5
12/3/87	9:29	6
12/3/87	10:29	7
12/3/87	11:29	11
12/3/87	12:29	7
12/3/87	13:29	6
12/3/87	14:29	14
12/3/87	15:29	15
12/3/87	16:29	19
12/3/87	17:29	16
12/3/87	18:29	8
12/3/87	19:29	7
12/3/87	20:29	6
12/3/87	21:29	4
12/3/87	22:29	4
12/3/87	23:29	3
12/10/87	0:35	1
12/10/87	1:35	0
12/10/87	2:35	0

	BURBANK	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
12/10/87	3:35	0
12/10/87	4:35	0
12/10/87	5:35	0
12/10/87	6:35	1
12/10/87	7:35	0
12/10/87	8:35	0
12/10/87	9:35	0
12/10/87	10:35	3
12/10/87	11:35	4
12/10/87	12:35	8
12/10/87	13:35	11
12/10/87	14:35	6
12/10/87	15:35	4
12/10/87	16:35	4
12/10/87	17:35	4
12/10/87	18:35	2
12/10/87	19:35	2
12/10/87	20:35	1
12/10/87	21:26	1
12/10/87	22:26	0
12/10/87	23:26	2
12/11/87	0:26	2
12/11/87	1:26	2
12/11/87	2:26	2
12/11/87	3:26	2
12/11/87	4:26	2
12/11/87	5:26	0
12/11/87	6:26	1
12/11/87	7:26	0
12/11/87	8:26	1
12/11/87	9:26	2
12/11/87	10:26	2
12/11/87	11:26	4
12/11/87	12:26	5
12/11/87	13:26	11
12/11/87	14:26	11
12/11/87	15:26	11
12/11/87	16:26	14
12/11/87	17:26	7
12/11/87	18:26	6
12/11/87	19:26	3
12/11/87	20:26	2
12/11/87	21:26	1

	BURBANK	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
12/11/87	22:26	1
12/11/87	23:26	0

	CLAREMONT	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
6/19/87		ND
6/23/87	22:11	0
6/24/87	23:11	≤5
6/24/87	0:11	0
6/24/87	1:11	0
6/24/87	2:11	≤5
6/24/87	3:11	0
6/24/87	4:11	0
6/24/87	5:11	0
6/24/87	6:11	0
6/24/87	7:11	1
6/24/87	8:11	≤5
6/24/87	9:11	≤5
6/24/87	10:11	2
6/24/87	11:11	7
6/24/87	12:11	5
6/24/87	13:11	4
6/24/87	14:11	5
6/24/87	15:11	5
6/24/87	16:11	≤5
6/24/87	17:11	≤5
6/24/87	18:11	1
6/24/87	19:11	3
6/24/87	20:11	0
6/24/87	21:11	3
6/24/87	22:11	≤5
6/24/87	23:11	≤5
6/25/87	0:11	≤3
6/25/87	1:11	≤5
6/25/87	2:11	≤3
6/25/87	3:11	0
6/25/87	4:11	7
6/25/87	5:11	0
6/25/87	6:11	2
6/25/87	7:11	3
6/25/87	8:11	3
6/25/87	9:11	5
6/25/87	10:11	3
6/25/87	11:11	3
6/25/87	12:11	3
6/25/87	13:12	3
6/25/87	14:12	1
6/25/87	15:12	≤5
6/25/87	16:12	≤5

	CLAREMONT	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
6/25/87	17:12	≤5
6/25/87	18:12	0
6/25/87	19:12	≤5
6/25/87	20:12	5
6/25/87	21:12	5
6/25/87	22:12	4
6/25/87	23:12	≤5
6/26/87	0:12	≤5
7/13/87	0:12	1
7/13/87	1:12	≤4
7/13/87	2:12	≤4
7/13/87	3:12	≤4
7/13/87	4:13	ND
7/13/87	5:13	ND
7/13/87	6:13	≤5
7/13/87	7:13	≤5
7/13/87	8:13	5
7/13/87	9:13	≤5
7/13/87	10:13	≤5
7/13/87	11:13	≤5
7/13/87	12:13	≤5
7/13/87	13:13	9
7/13/87	14:13	11
7/13/87	15:13	8
7/13/87	16:13	5
7/13/87	17:13	3
7/13/87	18:13	2
7/13/87	19:13	≤2
7/13/87	20:13	≤5
7/13/87	21:13	ND
7/13/87	22:13	≤5
7/13/87	23:13	≤5
7/14/87	0:13	ND
7/14/87	1:13	≤5
7/14/87	2:13	≤5
7/14/87	3:13	ND
7/14/87	4:13	≤5
7/14/87	5:13	ND
7/14/87	6:13	≤5
7/14/87	7:13	≤5
7/14/87	8:13	≤5
7/14/87	9:13	3
7/14/87	10:13	≤5
7/14/87	11:13	≤5
7/14/87	12:13	≤5

	CLAREMONT	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
7/14/87	13:13	4
7/14/87	14:13	9
7/14/87	15:13	11
7/14/87	16:13	8
7/14/87	17:13	5
7/14/87	18:13	≤5
7/14/87	19:56	≤5
7/14/87	20:56	≤3
7/14/87	21:56	2
7/14/87	22:56	≤1
7/14/87	23:56	ND
7/15/87	0:56	ND
7/15/87	1:56	0
7/15/87	2:57	≤5
7/15/87	3:57	≤5
7/15/87	4:57	≤3
7/15/87	5:57	≤3
7/15/87	6:57	0
7/15/87	7:57	2
7/15/87	8:57	3
7/15/87	9:57	4
7/15/87	10:57	4
7/15/87	11:57	4
7/15/87	12:57	8
7/15/87	13:57	9
7/15/87	14:57	8
7/15/87	15:57	6
7/15/87	16:57	7
7/15/87	17:57	6
7/15/87	18:57	4
7/15/87	19:57	≤3
7/15/87	20:57	0
7/15/87	21:57	0
7/15/87	22:57	0
8/26/87	23:03	2
8/27/87	1:30	3
8/27/87	2:30	4
8/27/87	3:30	4
8/27/87	4:30	5
8/27/87	5:30	4
8/27/87	6:30	4
8/27/87	7:30	6
8/27/87	8:30	5
8/27/87	9:30	9
8/27/87	11:01	10

	CLAREMONT	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
8/27/87	12:37	15
8/27/87	13:37	22
8/27/87	14:24	19
8/27/87	15:08	17
8/27/87	16:06	15
8/27/87	16:46	12
8/27/87	19:16	3
8/27/87	20:05	3
8/27/87	20:49	2
8/27/87	21:49	2
8/27/87	22:49	2
8/27/87	23:49	1
8/28/87	0:49	2
8/28/87	1:49	2
8/28/87	2:49	2
8/28/87	3:49	5
8/28/87	4:49	6
8/28/87	5:49	4
8/28/87	9:36	6
8/28/87	10:36	7
8/28/87	11:36	13
8/28/87	12:21	16
8/28/87	13:07	22
8/28/87	14:07	26
8/28/87	15:07	30
8/28/87	16:07	19
8/28/87	16:54	13
8/28/87	17:45	11
8/28/87	20:05	4
8/28/87	21:05	4
8/28/87	22:05	3
8/28/87	23:05	3
8/29/87	0:05	2
8/29/87	1:05	1
8/29/87	2:05	7
8/29/87	3:05	8
8/29/87	4:05	2
8/29/87	5:05	3
8/29/87	6:05	3
8/29/87	7:05	5
8/29/87	8:05	3
8/29/87	9:05	5
8/29/87	10:05	7
8/29/87	11:05	11
8/29/87	12:05	18

	CLAREMONT	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
8/29/87	13:05	22
8/29/87	14:05	25
8/29/87	15:06	25
8/29/87	16:06	27
8/29/87	17:06	26
8/29/87	18:06	19
8/29/87	19:06	15
8/29/87	20:06	10
8/29/87	21:06	7
8/29/87	22:06	4
8/29/87	23:06	4
Moved to Seaver Hall		
9/1/87	23:47	0
9/2/87	0:47	0
9/2/87	1:47	1
9/2/87	2:47	1
9/2/87	3:47	1
9/2/87	4:48	1
9/2/87	5:48	0
9/2/87	6:48	2
9/2/87	7:48	0
9/2/87	8:48	0
9/2/87	9:48	1
9/2/87	10:48	1
9/2/87	11:48	2
9/2/87	12:48	0
9/2/87	13:48	1
9/2/87	14:43	8
9/2/87	15:43	9
9/2/87	16:43	10
9/2/87	17:43	5
9/2/87	18:43	5
9/2/87	19:43	3
9/2/87	20:43	2
9/2/87	21:43	2
9/2/87	22:43	2
9/2/87	23:43	1
9/3/87	0:43	1
9/3/87	1:43	0
9/3/87	2:43	0
9/3/87	3:43	3
9/3/87	4:43	3
9/3/87	5:43	3
9/3/87	6:43	2

	CLAREMONT	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
9/3/87	7:43	3
9/3/87	8:43	4
9/3/87	9:43	8
9/3/87	10:43	7
9/3/87	11:43	8
9/3/87	12:43	10
9/3/87	13:43	5
9/3/87	14:43	4
9/3/87	15:43	4
9/3/87	16:43	3
9/3/87	17:43	2
9/3/87	18:43	1
9/3/87	19:43	0
9/3/87	20:43	0
9/3/87	21:43	0
9/3/87	22:43	0
9/3/87	23:43	0

	HAWTHORNE	
	PAN DATA	
Date	Time	PAN
	/PST	/ppbv
6/19/87	ND	0
6/24/87	12:52	≤9
6/24/87	13:52	≤9
6/24/87	14:52	≤9
6/24/87	15:52	≤9
6/24/87	16:52	≤9
6/24/87	17:52	≤9
6/24/87	18:52	≤9
6/24/87	20:46	≤4
6/24/87	21:46	≤9
6/24/87	22:46	≤4
6/24/87	23:46	≤4
6/25/87	0:46	≤9
6/25/87	1:46	≤4
6/25/87	2:46	≤4
6/25/87	3:46	≤4
6/25/87	4:46	≤9
6/25/87	5:46	≤4
6/25/87	6:46	≤4
6/25/87	7:46	≤4
6/25/87	8:46	≤4
6/25/87	9:46	≤4
6/25/87	10:46	≤4
6/25/87	11:46	≤4
6/25/87	12:46	≤9
6/25/87	13:46	≤9
6/25/87	14:46	≤9
6/25/87	15:46	≤4
6/25/87	16:46	≤9
6/25/87	17:46	≤9
6/25/87	18:46	≤4
6/25/87	19:46	≤9
6/25/87	20:46	≤9
6/25/87	21:46	≤4
6/25/87	22:46	≤9
6/25/87	23:46	≤4
7/12/87	23:49	≤2
7/13/87	0:49	≤2
7/13/87	1:49	≤2
7/13/87	2:49	≤2

	HAWTHORNE	
	PAN DATA	
Date	Time	PAN
	/PST	/ppbv
7/13/87	3:49	≤2
7/13/87	4:49	≤2
7/13/87	5:49	≤2
7/13/87	6:49	≤2
7/13/87	7:49	≤4
7/13/87	8:49	≤2
7/13/87	9:49	≤2
7/13/87	10:49	≤2
7/13/87	11:49	≤4
7/13/87	12:49	≤4
7/13/87	13:49	≤4
7/13/87	14:49	≤2
7/13/87	15:49	≤4
7/13/87	16:49	≤4
7/13/87	17:49	≤4
7/13/87	19:44	≤4
7/13/87	20:44	≤3
7/13/87	21:44	≤4
7/13/87	22:44	≤4
7/13/87	23:44	≤3
7/14/87	0:44	≤3
7/14/87	1:44	≤4
7/14/87	2:44	≤4
7/14/87	3:44	≤3
7/14/87	4:44	≤3
7/14/87	5:44	≤3
7/14/87	6:44	≤3
7/14/87	7:44	≤4
7/14/87	8:44	≤4
7/14/87	9:44	≤9
7/14/87	10:44	ND
7/14/87	11:44	ND
7/14/87	12:44	≤9
7/14/87	13:44	≤9
7/14/87	14:44	ND
7/14/87	15:44	ND
7/14/87	16:44	≤4
7/14/87	17:44	≤4
7/14/87	18:45	ND
7/14/87	19:45	≤4
7/14/87	20:45	≤2
7/14/87	21:45	≤4

HAWTHORNE PAN DATA		
Date	Time /PST	PAN /ppbv
7/14/87	22:45	≤2
7/14/87	23:45	≤2
7/15/87	0:45	≤2
7/15/87	1:45	≤2
7/15/87	2:45	≤4
7/15/87	3:45	≤9
7/15/87	4:45	≤4
7/15/87	5:45	≤2
7/15/87	6:45 - 22:45	ND
11/11/87	0:03	0
11/11/87	0:33	0
11/11/87	1:03	0
11/11/87	1:33	0
11/11/87	2:03	0
11/11/87	2:33	0
11/11/87	3:03	0
11/11/87	3:33	0
11/11/87	4:03	1
11/11/87	4:33	1
11/11/87	5:03	0
11/11/87	5:33	0
11/11/87	6:03	0
11/11/87	6:33	0
11/11/87	7:03	0
11/11/87	7:33	0
11/11/87	8:03	0
11/11/87	8:33	0
11/11/87	9:03	0
11/11/87	9:33	0
11/11/87	10:03	0
11/11/87	10:33	0
11/11/87	11:03	0
11/11/87	11:33	≤2
11/11/87	12:03	1
11/11/87	12:33	2
11/11/87	13:03	≤2
11/11/87	13:33	1
11/11/87	14:03	≤2
11/11/87	14:33	1
11/11/87	15:03	≤2
11/11/87	15:33	≤2
11/11/87	16:03	≤2

HAWTHORNE PAN DATA		
Date	Time /PST	PAN /ppbv
11/11/87	16:33	≤2
11/11/87	17:03	1
11/11/87	17:33	0
11/11/87	18:03	0
11/11/87	18:33	0
11/11/87	19:03	0
11/11/87	19:33	0
11/11/87	20:03	0
11/11/87	20:33	≤2
11/11/87	21:03	0
11/11/87	21:33	0
11/11/87	22:03	0
11/11/87	22:33	0
11/11/87	23:03	0
11/11/87	23:33	≤2
11/12/87	0:03	0
11/12/87	0:33	0
11/12/87	1:03	0
11/12/87	1:33	0
11/12/87	2:03	0
11/12/87	2:33	0
11/12/87	3:03	0
11/12/87	3:33	0
11/12/87	4:03	0
11/12/87	4:33	0
11/12/87	5:03	0
11/12/87	5:33	0
11/12/87	6:03	0
11/12/87	6:33	1
11/12/87	7:03	1
11/12/87	7:33	0
11/12/87	8:03	≤2
11/12/87	8:33	1
11/12/87	9:03	≤2
11/12/87	9:33	≤2
11/12/87	10:03	4
11/12/87	10:33	ND
11/12/87	12:01	5
11/12/87	13:01	4
11/12/87	13:30	6
11/12/87	14:01	6
11/12/87	14:30	9

	HAWTHORNE	
	PAN DATA	
Date	Time	PAN
	/PST	/ppbv
11/12/87	15:01	8
11/12/87	15:30	7
11/12/87	16:01	4
11/12/87	16:36	5
11/12/87	17:30	4
11/12/87	17:30	2
11/12/87	18:01	0
11/12/87	18:30	1
11/12/87	19:01	1
11/12/87	19:30	1
11/12/87	20:01	0
11/12/87	20:30	0
11/12/87	21:01	1
11/12/87	21:30	1
11/12/87	22:01	1
11/12/87	22:30	1
11/12/87	23:01	1
11/12/87	23:30	1
11/13/87	0:01	0
11/13/87	0:30	1
11/13/87	1:01	≤1
11/13/87	1:30	1
11/13/87	2:01	0
11/13/87	2:30	1
11/13/87	3:01	0
11/13/87	3:30	0
11/13/87	4:01	1
11/13/87	4:30	1
11/13/87	5:01	2
11/13/87	5:30	1
11/13/87	6:01	1
11/13/87	6:30	1
11/13/87	7:01	2
11/13/87	7:30	2
11/13/87	8:01	2
11/13/87	8:30	2
11/13/87	9:01	2
11/13/87	9:30	2
11/13/87	10:01	3
11/13/87	10:30	2
11/13/87	11:01	3
11/13/87	11:30	3

	HAWTHORNE	
	PAN DATA	
Date	Time	PAN
	/PST	/ppbv
11/13/87	12:01	2
11/13/87	12:30	3
11/13/87	13:01	4
11/13/87	13:30	3
11/13/87	14:01	3
11/13/87	13:25	3
11/13/87	13:55	2
11/13/87	14:25	1
11/13/87	14:55	1
11/13/87	15:25	1
11/13/87	15:33	1
11/13/87	16:25	2
11/13/87	16:55	1
11/13/87	17:25	2
11/13/87	17:55	0
11/13/87	18:25	1
11/13/87	18:55	0
11/13/87	19:25	1
11/13/87	19:55	0
11/13/87	20:25	0
11/13/87	20:55	0
11/13/87	21:25	1
11/13/87	21:55	0
11/13/87	22:25	0
11/13/87	22:55	0
11/13/87	23:25	0
11/13/87	23:33	0
11/14/87	0:25	0
12/3/87	0:47	0
12/3/87	1:47	1
12/3/87	2:47	3
12/3/87	3:47	2
12/3/87	4:47	2
12/3/87	5:47	2
12/3/87	6:47	3
12/3/87	7:47	3
12/3/87	8:47	3
12/3/87	9:47	7
12/3/87	10:47	10
12/3/87	11:47	13
12/3/87	12:47	16
12/3/87	13:47	13



	HAWTHORNE	
	PAN DATA	
Date	Time	PAN
	/PST	/ppbv
12/3/87	14:47	12
12/3/87	15:47	15
12/3/87	16:47	4
12/3/87	17:47	3
12/3/87	18:47	4
12/3/87	19:47	2
12/3/87	20:47	1
12/3/87	21:47	1
12/3/87	22:47	1
12/4/87	0:14	1
12/9/87	18:01	2
12/9/87	19:01	2
12/9/87	20:01	1
12/9/87	21:01	1
12/9/87	22:01	0
12/9/87	23:01	0
12/10/87	0:01	1
12/10/87	1:01	1
12/10/87	2:01	1
12/10/87	3:01	1
12/10/87	4:01	1
12/10/87	5:01	0
12/10/87	6:01	1
12/10/87	7:01	1
12/10/87	8:01	1
12/10/87	9:01	1
12/10/87	10:01	2
12/10/87	11:01	4
12/10/87	12:01	3
12/10/87	13:01	4
12/10/87	14:34	3
12/10/87	15:34	1
12/10/87	16:34	ND
12/10/87	17:34	0
12/10/87	18:34	≤2
12/10/87	19:34	≤2
12/10/87	20:34	1
12/10/87	21:31	0
12/10/87	22:34	0
12/10/87	23:34	0
12/11/87	0:34	0
12/11/87	1:34	≤1

	HAWTHORNE	
	PAN DATA	
Date	Time	PAN
	/PST	/ppbv
12/11/87	2:34	0
12/11/87	3:34	0
12/11/87	4:34	2
12/11/87	5:34	1
12/11/87	6:34	1
12/11/87	7:34	1
12/11/87	8:34	1
12/11/87	9:34	3
12/11/87	10:34	4
12/11/87	11:34	5
12/11/87	12:34	5
12/11/87	13:34	5
12/11/87	14:34	9
12/11/87	15:34	3
12/11/87	16:34	3
12/11/87	17:34	3
12/11/87	18:34	2
12/11/87	19:34	1
12/11/87	20:34	2
12/11/87	21:34	2
12/11/87	22:34	0
12/11/87	23:34	≤1
12/12/87	0:34	0

	LONG BEACH	
	PAN DATA	
Date	Time /PST	PAN /ppbv
6/19/87	0:00	ND
6/24/87	14:00	ND
6/24/87	15:05	≤3
6/24/87	16:05	≤3
6/24/87	17:05	≤3
6/24/87	18:05	≤3
6/24/87	19:05	≤5
6/24/87	20:05	≤5
6/24/87	21:05	≤3
6/24/87	22:05	≤3
6/24/87	23:05	≤5
6/25/87	0:05	≤5
6/25/87	1:05	≤3
6/25/87	2:05	≤3
6/25/87	3:05	≤3
6/25/87	4:05	≤3
6/25/87	5:05	2
6/25/87	6:05	≤3
6/25/87	7:05	3
6/25/87	8:05	≤3
6/25/87	9:05	3
6/25/87	10:05	ND
6/25/87	11:13	4
6/25/87	12:20	0
6/25/87	13:20	3
6/25/87	14:20	3
6/25/87	17:36	≤3
6/25/87	18:36	≤3
6/25/87	19:36	≤3
6/25/87	20:36	2
6/25/87	21:36	≤3
6/25/87	22:36	2
6/25/87	23:36	≤3
6/26/87	0:36	1
7/12/87	22:44	≤3
7/12/87	23:44	≤3
7/13/87	0:44	≤3
7/13/87	1:44	≤3
7/13/87	2:44	≤3
7/13/87	3:44	≤3
7/13/87	4:44	≤3
7/13/87	5:44	≤5
7/13/87	6:44	≤3

	LONG BEACH	
	PAN DATA	
Date	Time /PST	PAN /ppbv
7/13/87	7:44	≤5
7/13/87	8:44	≤5
7/13/87	9:44	≤5
7/13/87	10:44	≤3
7/13/87	11:44	3
7/13/87	12:44	2
7/13/87	15:12	2
7/13/87	15:54	0
7/13/87	16:54	0
7/13/87	17:54	≤2
7/13/87	18:54	≤2
7/13/87	19:54	≤2
7/13/87	20:54	≤2
7/13/87	21:55	≤3
7/13/87	22:55	≤2
7/13/87	23:55	≤2
7/14/87	0:55	≤3
7/14/87	1:55	≤2
7/14/87	2:55	≤2
7/14/87	3:55	≤2
7/14/87	4:55	≤2
7/14/87	5:55	≤2
7/14/87	6:55	≤2
7/14/87	7:55	≤2
7/14/87	8:55	≤3
7/14/87	9:55	2
7/14/87	10:55	2
7/14/87	11:55	4
7/14/87	12:55	3
7/14/87	13:55	4
7/14/87	14:55	3
7/14/87	15:55	2
7/14/87	16:55	≤2
7/14/87	17:55	≤2
7/14/87	18:55	0
7/14/87	19:55	1
7/14/87	20:55	0
7/14/87	21:55	0
7/14/87	22:55	1
7/14/87	23:55	0
7/15/87	0:55	0
7/15/87	1:55	0
7/15/87	2:55	≤1

	LONG BEACH	
	PAN DATA	
Date	Time /PST	PAN /ppbv
7/15/87	3:55	≤1
7/15/87	4:55	0
7/15/87	5:55	0
7/15/87	6:55	0
7/15/87	7:55	0
7/15/87	8:55	1
7/15/87	9:55	≤2
7/15/87	10:55	≤3
7/15/87	11:55	1
7/15/87	12:55	≤3
7/15/87	13:55	≤3
7/15/87	14:55	1
7/15/87	15:55	3
7/15/87	16:55	0
7/15/87	17:55	1
7/15/87	18:55	1
7/15/87	19:55	1
7/15/87	20:55	≤2
7/15/87	21:55	≤2
7/15/87	22:55	0
7/15/87	23:55	1
8/27/87	0:03	ND
8/27/87	1:03	2
8/27/87	2:03	0
8/27/87	3:03	0
8/27/87	4:03	0
8/27/87	5:03	0
8/27/87	6:03	0
8/27/87	7:03	0
8/27/87	8:03	3
8/27/87	9:03	4
8/27/87	10:30	4
8/27/87	11:03	3
8/27/87	12:03	4
8/27/87	13:03	4
8/27/87	14:03	5
8/27/87	15:03	3
8/27/87	16:03	2
8/27/87	17:03	3
8/27/87	18:03	3
8/27/87	19:03	0
8/27/87	20:03	2
8/27/87	21:03	0

	LONG BEACH	
	PAN DATA	
Date	Time /PST	PAN /ppbv
8/27/87	22:03	2
8/27/87	23:03	2
8/28/87	0:03	0
8/28/87	1:03	2
8/28/87	2:03	2
8/28/87	3:03	0
8/28/87	4:03	0
8/28/87	5:03	0
8/28/87	6:04	0
8/28/87	7:04	2
8/28/87	8:04	2
8/28/87	9:04	3
8/28/87	10:04	4
8/28/87	11:04	8
8/28/87	12:04	7
8/28/87	13:04	8
8/28/87	14:04	5
8/28/87	15:04	4
8/28/87	16:04	4
8/28/87	17:04	4
8/28/87	18:04	3
8/28/87	19:04	2
8/28/87	20:04	2
8/28/87	21:04	2
8/28/87	22:04	2
8/28/87	23:04	2
8/29/87	0:04	3
8/29/87	1:04	4
8/29/87	2:04	3
8/29/87	3:04	3
8/29/87	4:04	3
8/29/87	5:04	3
8/29/87	6:04	3
8/29/87	7:04	3
8/29/87	8:04	3
8/29/87	9:04	2
8/29/87	10:04	3
8/29/87	11:04	3
8/29/87	12:04	4
8/29/87	13:04	6
8/29/87	14:04	4
8/29/87	15:04	3
8/29/87	16:04	4

	LONG BEACH	
	PAN DATA	
Date	Time /PST	PAN /ppbv
8/29/87	17:04	3
8/29/87	18:04	ND
8/29/87	19:04	2
8/29/87	20:04	0
8/29/87	21:04	0
8/29/87	22:04	0
8/29/87	23:04	0
8/30/87	0:04	0
9/2/87	0:21	0
9/2/87	1:21	0
9/2/87	2:21	0
9/2/87	3:21	0
9/2/87	4:21	0
9/2/87	5:21	0
9/2/87	6:21	0
9/2/87	7:21	0
9/2/87	8:21	3
9/2/87	9:21	5
9/2/87	10:21	6
9/2/87	11:21	11
9/2/87	12:21	16
9/2/87	13:21	3
9/2/87	14:21	3
9/2/87	15:21	3
9/2/87	16:21	2
9/2/87	17:22	2
9/2/87	18:22	2
9/2/87	19:22	0
9/2/87	20:22	0
9/2/87	21:22	0
9/2/87	22:22	0
9/2/87	23:22	0
9/3/87	0:22	0
9/3/87	1:22	0
9/3/87	2:22	0
9/3/87	3:22	0
9/3/87	4:22	1
9/3/87	5:22	2
9/3/87	6:22	1
9/3/87	7:22	2
9/3/87	8:22	3
9/3/87	9:22	2
9/3/87	10:22	3

	LONG BEACH	
	PAN DATA	
Date	Time /PST	PAN /ppbv
9/3/87	11:22	2
9/3/87	12:22	2
9/3/87	13:22	0
9/3/87	14:22	1
9/3/87	15:22	1
9/3/87	16:22	1
9/3/87	17:22	0
9/3/87	18:22	0
9/3/87	19:22	0
9/3/87	20:22	0
9/3/87	21:22	0
9/3/87	22:22	0
9/3/87	23:22	0
9/4/87	0:22	0
11/11/87	8:01	0
11/11/87	8:56	0
11/11/87	9:52	2
11/11/87	10:49	2
11/11/87	11:49	2
11/11/87	12:49	3
11/11/87	13:49	3
11/11/87	14:49	4
11/11/87	15:49	3
11/11/87	16:49	3
11/11/87	17:49	0
11/11/87	18:49	1
11/11/87	19:49	0
11/11/87	20:49	0
11/11/87	21:49	0
11/11/87	22:49	0
11/11/87	23:49	0
11/12/87	0:49	0
11/12/87	1:49	0
11/12/87	2:49	0
11/12/87	3:49	0
11/12/87	4:49	0
11/12/87	5:50	0
11/12/87	6:50	0
11/12/87	7:50	0
11/12/87	8:50	1
11/12/87	9:50	2
11/12/87	10:50	4
11/12/87	11:50	4

	LONG BEACH	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
11/12/87	12:50	6
11/12/87	13:50	7
11/12/87	14:50	7
11/12/87	15:50	5
11/12/87	16:50	6
11/12/87	17:50	2
11/12/87	18:50	3
11/12/87	19:50	1
11/12/87	20:50	0
11/12/87	21:50	0
11/12/87	22:50	0
11/12/87	23:50	0
11/13/87	0:50	0
11/13/87	1:50	0
11/13/87	2:50	0
11/13/87	3:50	0
11/13/87	4:50	0
11/13/87	5:50	0
11/13/87	6:50	2
11/13/87	7:50	3
11/13/87	8:50	3
11/13/87	9:50	3
11/13/87	10:50	2
11/13/87	11:50	2
11/13/87	12:50	3
11/13/87	13:50	2
11/13/87	14:50	2
11/13/87	15:50	0
11/13/87	16:50	0
11/13/87	17:50	2
11/13/87	18:50	2
11/13/87	19:50	0
11/13/87	20:50	0
11/13/87	21:50	0
11/13/87	22:50	0
11/13/87	23:50	0
12/3/87	0:32	0
12/3/87	1:33	2
12/3/87	2:33	2
12/3/87	3:33	0
12/3/87	4:33	2
12/3/87	5:33	0
12/3/87	6:33	2

	LONG BEACH	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
12/3/87	7:33	0
12/3/87	8:33	2
12/3/87	9:33	4
12/3/87	10:33	5
12/3/87	11:33	8
12/3/87	12:33	9
12/3/87	13:33	12
12/3/87	14:33	15
12/3/87	15:33	14
12/3/87	16:33	13
12/3/87	17:33	10
12/3/87	18:33	6
12/3/87	19:33	5
12/3/87	20:33	3
12/3/87	21:33	2
12/3/87	22:33	2
12/3/87	23:33	2
12/10/87	0:15	0
12/10/87	1:15	0
12/10/87	2:15	0
12/10/87	3:15	2
12/10/87	4:15	0
12/10/87	5:15	1
12/10/87	6:15	0
12/10/87	7:15	0
12/10/87	8:15	0
12/10/87	9:15	2
12/10/87	10:15	4
12/10/87	11:15	4
12/10/87	12:15	4
12/10/87	13:15	7
12/10/87	14:15	7
12/10/87	15:15	8
12/10/87	16:15	3
12/10/87	17:15	0
12/10/87	18:15	0
12/10/87	19:16	0
12/10/87	20:16	0
12/10/87	21:16	0
12/10/87	22:16	0
12/10/87	23:16	0
12/11/87	0:16	0
12/11/87	1:16	0

	LONG BEACH	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
12/11/87	2:16	0
12/11/87	3:16	0
12/11/87	4:16	0
12/11/87	5:16	0
12/11/87	6:16	2
12/11/87	7:16	0
12/11/87	8:16	0
12/11/87	9:16	0
12/11/87	10:16	3
12/11/87	11:16	3
12/11/87	12:16	5
12/11/87	13:16	5
12/11/87	14:16	6
12/11/87	15:16	8
12/11/87	16:16	5
12/11/87	17:16	6
12/11/87	18:16	4
12/11/87	19:16	3
12/11/87	20:16	0
12/11/87	21:16	2
12/11/87	22:16	0
12/11/87	23:16	0

	LOS ANGELES	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
6/19/87		ND
6/23/87	23:53	≤7
6/24/87	0:53	5
6/24/87	1:53	3
6/24/87	2:53	≤4
6/24/87	3:53	≤4
6/24/87	4:53	4
6/24/87	5:53	≤7
6/24/87	6:53	3
6/24/87	7:53	3
6/24/87	8:53	5
6/24/87	9:53	6
6/24/87	10:53	7
6/24/87	11:53	9
6/24/87	11:43	6
6/24/87	13:53	6
6/24/87	14:53	6
6/24/87	15:53	3
6/24/87	17:07	3
6/24/87	18:07	ND
6/24/87	20:30	ND
6/24/87	21:30	ND
6/24/87	22:30	≤7
6/24/87	23:30	≤7
6/25/87	0:30	ND
6/25/87	1:30	ND
6/25/87	2:30	2
6/25/87	3:30	≤4
6/25/87	4:30	0
6/25/87	5:30	0
6/25/87	6:30	0
6/25/87	7:30	3
6/25/87	8:30	3
6/25/87	9:30	4
6/25/87	10:30	7
6/25/87	11:30	5
6/25/87	12:30	4
6/25/87	13:30	4
6/25/87	14:30	4
6/25/87	15:30	5
6/25/87	16:30	5
6/25/87	17:30	4

	LOS ANGELES	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
6/25/87	18:30	3
6/25/87	19:30	≤4
6/25/87	20:30	≤7
6/25/87	21:30	≤4
6/25/87	22:30	2
6/25/87	23:30	ND
6/26/87	0:30	≤7
7/12/87	23:16	≤4
7/13/87	0:16	ND
7/13/87	1:16	ND
7/13/87	2:16	ND
7/13/87	3:16	≤7
7/13/87	4:16	ND
7/13/87	5:16	≤7
7/13/87	6:16	ND
7/13/87	7:16	4
7/13/87	8:16	≤4
7/13/87	9:16	1
7/13/87	10:16	≤4
7/13/87	11:16	≤7
7/13/87	12:16	ND
7/13/87	13:16	ND
7/13/87	14:16	ND
7/13/87	15:16	ND
7/13/87	16:16	≤4
7/13/87	17:16	≤4
7/13/87	18:16 - 10:16	ND
7/14/87	11:16	≤7
7/14/87	12:16	≤7
7/14/87	13:16	≤7
7/14/87	14:16	ND
7/14/87	15:16	≤7
7/14/87	16:16	≤7
7/14/87	17:16	≤7
7/14/87	18:16	≤4
7/14/87	19:16	4
7/14/87	20:16	ND
7/14/87	21:16	ND
7/14/87	22:16	ND
7/14/87	23:16	ND
7/15/87	0:16	ND
7/15/87	1:16	≤7
7/15/87	2:16	≤7

	LOS ANGELES	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
7/15/87	3:16	≤7
7/15/87	4:16	ND
7/15/87	5:16	ND
7/15/87	6:16	≤7
7/15/87	7:16	≤7
7/15/87	8:16	≤7
7/15/87	9:16	ND
7/15/87	10:16	ND
7/15/87	11:16	≤7
7/15/87	12:16	≤7
7/15/87	13:16	2
7/15/87	14:16	≤7
7/15/87	15:16	≤7
7/15/87	16:16	≤7
7/15/87	17:16	ND
7/15/87	18:16	≤4
7/15/87	19:16	ND
7/15/87	20:16	ND
7/15/87	21:16	ND
7/15/87	22:16	2
7/15/87	23:16	≤7
8/27/87	0:02	1
8/27/87	1:02	0
8/27/87	2:02	≤1
8/27/87	3:02	≤1
8/27/87	4:02	1
8/27/87	5:02	≤1
8/27/87	6:02	1
8/27/87	7:02	≤2
8/27/87	8:02	2
8/27/87	9:02	4
8/27/87	10:02	6
8/27/87	11:02	4
8/27/87	12:02	5
8/27/87	13:02	5
8/27/87	14:02	4
8/27/87	15:02	2
8/27/87	16:02	2
8/27/87	17:02	2
8/27/87	18:02	≤2
8/27/87	19:02	1
8/27/87	20:02	1
8/27/87	21:02	1

	LOS ANGELES	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
8/27/87	22:02	1
8/27/87	23:02	≤2
8/28/87	0:02	≤2
8/28/87	1:02	≤2
8/28/87	2:02	0
8/28/87	3:02	≤2
8/28/87	4:02	0
8/28/87	5:02	≤2
8/28/87	6:02	0
8/28/87	7:02	1
8/28/87	8:02	1
8/28/87	9:02	3
8/28/87	10:02	6
8/28/87	11:02	10
8/28/87	12:02	6
8/28/87	13:02	6
8/28/87	14:02	7
8/28/87	15:02	6
8/28/87	16:02	4
8/28/87	17:02	2
8/28/87	18:02	2
8/28/87	19:02	1
8/28/87	20:02	1
8/28/87	21:02	1
8/28/87	22:02	1
8/28/87	23:02	≤2
8/29/87	0:02	1
8/29/87	1:02	1
8/29/87	2:02	1
8/29/87	3:02	1
8/29/87	4:02	1
8/29/87	5:02	1
8/29/87	6:02	1
8/29/87	7:02	≤1
8/29/87	8:02	2
8/29/87	9:02	2
8/29/87	10:02	5
8/29/87	11:02	8
8/29/87	12:02	8
8/29/87	13:02	8
8/29/87	14:02	8
8/29/87	15:02	11
8/29/87	16:02	8



	LOS ANGELES	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
8/29/87	17:02	4
8/29/87	18:02	4
8/29/87	19:02	3
8/29/87	20:02	2
8/29/87	21:02	2
8/29/87	22:02	1
8/29/87	23:02	1
8/30/87	0:02	1
9/2/87	0:02	0
9/2/87	1:02	0
9/2/87	2:02	0
9/2/87	3:02	0
9/2/87	4:02	0
9/2/87	5:02	0
9/2/87	6:02	0
9/2/87	7:02	1
9/2/87	8:03	1
9/2/87	9:03	1
9/2/87	10:03	3
9/2/87	11:03	6
9/2/87	12:03	8
9/2/87	13:03	4
9/2/87	14:03	4
9/2/87	15:03	2
9/2/87	16:03	1
9/2/87	17:03	1
9/2/87	18:03	2
9/2/87	19:03	1
9/2/87	20:03	1
9/2/87	21:03	1
9/2/87	22:03	1
9/2/87	23:03	0
9/3/87	0:03	0
9/3/87	1:03	0
9/3/87	2:03	0
9/3/87	3:03	0
9/3/87	4:03	0
9/3/87	5:03	0
9/3/87	6:03	0
9/3/87	7:03	0
9/3/87	8:03	1
9/3/87	9:03	2
9/3/87	10:03	3

	LOS ANGELES	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
9/3/87	11:03	4
9/3/87	12:03	4
9/3/87	13:03	4
9/3/87	14:03	3
9/3/87	15:03	2
9/3/87	16:03	2
9/3/87	17:03	1
9/3/87	18:03	≤2
9/3/87	19:03	≤2
9/3/87	20:03	1
9/3/87	21:03	≤2
9/3/87	22:03	0
9/3/87	23:03	0
9/4/87	0:03	0
11/11/87	0:14	1
11/11/87	1:14	0
11/11/87	2:14	0
11/11/87	3:14	1
11/11/87	4:14	0
11/11/87	5:14	0
11/11/87	6:14	0
11/11/87	7:14	0
11/11/87	8:14	0
11/11/87	9:14	1
11/11/87	10:14	0
11/11/87	11:14	1
11/11/87	12:14	2
11/11/87	13:14	2
11/11/87	14:14	2
11/11/87	15:14	2
11/11/87	16:14	4
11/11/87	17:14	1
11/11/87	18:14	1
11/11/87	19:14	1
11/11/87	20:14	0
11/11/87	21:14	0
11/11/87	22:14	0
11/11/87	23:15	1
11/12/87	0:15	1
11/12/87	1:15	0
11/12/87	2:15	0
11/12/87	3:15	1
11/12/87	4:15	1

	LOS ANGELES	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
11/12/87	5:15	1
11/12/87	6:15	1
11/12/87	7:15	1
11/12/87	8:15	0
11/12/87	9:15	1
11/12/87	10:15	2
11/12/87	11:15	3
11/12/87	12:15	4
11/12/87	13:15	8
11/12/87	14:15	10
11/12/87	15:15	9
11/12/87	16:15	8
11/12/87	17:15	5
11/12/87	18:15	4
11/12/87	19:15	2
11/12/87	20:15	0
11/12/87	21:15	1
11/12/87	22:15	0
11/12/87	23:15	1
11/13/87	0:15	1
11/13/87	2:15	1
11/13/87	3:15	1
11/13/87	4:15	1
11/13/87	5:15	2
11/13/87	6:15	1
11/13/87	7:15	2
11/13/87	8:15	2
11/13/87	9:15	3
11/13/87	10:15	2
11/13/87	11:15	3
11/13/87	12:15	6
11/13/87	13:15	7
11/13/87	14:15	7
11/13/87	15:15	4
11/13/87	16:15	4
11/13/87	17:15	3
11/13/87	18:15	1
11/13/87	19:15	0
11/13/87	20:15	1
11/13/87	21:15	1
11/13/87	22:15	1
11/13/87	23:15	1
11/14/87	0:15	1

	LOS ANGELES	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
12/3/87	0:12	4
12/3/87	1:12	4
12/3/87	2:12	4
12/3/87	3:12	5
12/3/87	4:12	4
12/3/87	5:12	4
12/3/87	6:12	4
12/3/87	7:12	5
12/3/87	8:12	4
12/3/87	9:12	4
12/3/87	10:12	4
12/3/87	11:12	6
12/3/87	12:12	4
12/3/87	13:12	4
12/3/87	14:12	12
12/3/87	15:12	12
12/3/87	16:12	13
12/3/87	17:12	8
12/3/87	18:12	5
12/3/87	19:12	3
12/3/87	20:12	3
12/3/87	21:12	3
12/3/87	22:12	3
12/3/87	23:12	3
12/4/87	0:12	3
12/10/87	0:30	1
12/10/87	1:30	1
12/10/87	2:30	0
12/10/87	3:30	0
12/10/87	4:30	0
12/10/87	5:30	0
12/10/87	6:30	0
12/10/87	7:30	0
12/10/87	8:30	0
12/10/87	9:30	1
12/10/87	10:30	1
12/10/87	11:30	3
12/10/87	12:30	4
12/10/87	13:30	6
12/10/87	14:30	3
12/10/87	15:30	4
12/10/87	16:31	3
12/10/87	17:31	1

	LOS ANGELES	
	PAN DATA	
	Time	PAN
Date	/PST	/ppbv
12/10/87	18:31	1
12/10/87	19:31	1
12/10/87	20:31	1
12/10/87	21:31	1
12/10/87	22:31	2
12/10/87	23:31	1
12/11/87	0:31	0
12/11/87	1:31	1
12/11/87	2:31	1
12/11/87	3:31	1
12/11/87	4:31	1
12/11/87	5:31	1
12/11/87	6:31	1
12/11/87	7:31	0
12/11/87	8:31	1
12/11/87	9:31	1
12/11/87	10:31	2
12/11/87	11:31	4
12/11/87	12:31	5
12/11/87	13:31	7
12/11/87	14:31	8
12/11/87	15:31	9
12/11/87	16:31	6
12/11/87	17:31	5
12/11/87	18:31	4
12/11/87	19:31	3
12/11/87	20:31	2
12/11/87	21:31	1
12/11/87	22:31	1
12/11/87	23:31	0

	RUBIDOUX PAN DATA	
Date	Time	PAN
	/PST	/ppbv
6/19/87	ND	ND
6/24/87	6:28	0
6/24/87	7:28	0
6/24/87	8:28	0
6/24/87	9:28	0
6/24/87	10:28	4
6/24/87	11:28	4
6/24/87	12:29	ND
6/24/87	13:29	7
6/24/87	14:29	5
6/24/87	5:57	5
6/24/87	16:29	4
6/24/87	17:29	4
6/24/87	18:29	ND
6/24/87	19:29	0
6/24/87	20:29	0
6/24/87	21:29	0
6/24/87	22:29	ND
6/24/87	23:29	0
6/25/87	0:29	ND
6/25/87	1:29	ND
6/25/87	2:29	0
6/25/87	3:29	ND
6/25/87	4:29	ND
6/25/87	5:29	ND
6/25/87	6:29	0
6/25/87	7:29	0
6/25/87	8:29	ND
6/25/87	9:29	ND
6/25/87	10:29	ND
6/25/87	11:29	ND
6/25/87	12:29	ND
6/25/87	13:29	5
6/25/87	14:29	4
6/25/87	15:29	7
6/25/87	16:29	4
6/25/87	17:29	0
6/25/87	18:29	ND
6/25/87	19:29	4
6/25/87	20:29	ND
6/25/87	21:29	ND

	RUBIDOUX PAN DATA	
Date	Time	PAN
	/PST	/ppbv
6/25/87	22:29	ND
6/25/87	23:29	ND
6/26/87	0:29	ND
7/12/87	23:57	ND
7/13/87	0:57	0
7/13/87	1:57	0
7/13/87	2:57	0
7/13/87	3:57	ND
7/13/87	4:57	ND
7/13/87	5:58	0
7/13/87	6:58	0
7/13/87	7:58	4
7/13/87	8:58	0
7/13/87	9:58	0
7/13/87	10:58	4
7/13/87	11:58	4
7/13/87	12:58	5
7/13/87	13:58	5
7/13/87	14:58	5
7/13/87	15:58	5
7/13/87	16:58	4
7/13/87	17:58	0
7/13/87	18:58	0
7/13/87	19:58	0
7/13/87	20:58	0
7/13/87	21:58	0
7/13/87	22:58	0
7/13/87	23:58	0
7/14/87	0:58	ND
7/14/87	1:58	ND
7/14/87	2:58	ND
7/14/87	3:58	ND
7/14/87	4:58	0
7/14/87	5:58	ND
7/14/87	6:58	0
7/14/87	7:58	ND
7/14/87	8:58	ND
7/14/87	9:58	ND
7/14/87	10:58	0
7/14/87	11:58	ND
7/14/87	12:58	4
7/14/87	13:58	5
7/14/87	14:58	5

RUBIDOUX PAN DATA		
Date	Time /PST	PAN /ppbv
7/14/87	16:48	9
7/14/87	17:42	9
7/14/87	18:42	5
7/14/87	19:42	5
7/14/87	20:42	0
7/14/87	21:42	ND
7/14/87	22:42	ND
7/14/87	23:42	0
7/15/87	0:42	ND
7/15/87	1:42	ND
7/15/87	2:42	ND
7/15/87	3:42	ND
7/15/87	4:42	≤6
7/15/87	5:42	0
7/15/87	6:42	0
7/15/87	7:42	ND
7/15/87	8:42	0
7/15/87	9:42	5
7/15/87	10:42	9
7/15/87	11:42	7
7/15/87	12:42	7
7/15/87	13:42	5
7/15/87	14:42	5
7/15/87	15:42	ND
7/15/87	16:42	ND
7/15/87	17:42	5
7/15/87	18:42	4
7/15/87	19:42	0
7/15/87	20:42	0
7/15/87	21:42	0
7/15/87	22:42	0
7/15/87	23:42	0
7/16/87	0:42	ND
8/26/87	19:15	0
8/26/87	20:15	5
8/26/87	21:15	5
8/26/87	22:15	3
8/26/87	23:15	3
8/27/87	0:15	1
8/27/87	1:15	3
8/27/87	2:15	3
8/27/87	3:15	2
8/27/87	4:15	1

RUBIDOUX PAN DATA		
Date	Time /PST	PAN /ppbv
8/27/87	5:15	1
8/27/87	6:15	≤5
8/27/87	7:15	0
8/27/87	8:15	4
8/27/87	9:15	6
8/27/87	10:15	7
8/27/87	11:15	8
8/27/87	12:15	7
8/27/87	13:15	9
8/27/87	14:15	14
8/27/87	15:15	9
8/27/87	16:15	7
8/27/87	17:15	5
8/27/87	18:15	7
8/27/87	19:15	5
8/27/87	20:15	3
8/27/87	21:15	3
8/27/87	22:15	2
8/27/87	23:15	0
8/28/87	0:15	2
8/28/87	1:15	3
8/28/87	2:16	3
8/28/87	3:16	3
8/28/87	4:16	3
8/28/87	5:16	1
8/28/87	6:16	2
8/28/87	7:16	2
8/28/87	8:16	4
8/28/87	9:56	6
8/28/87	10:57	7
8/28/87	11:57	6
8/28/87	12:57	5
8/28/87	13:57	10
8/28/87	14:57	13
8/28/87	15:57	11
8/28/87	16:57	11
8/28/87	17:57	9
8/28/87	18:57	7
8/28/87	19:57	5
8/28/87	20:57	5
8/28/87	21:57	5
8/28/87	22:57	3
8/28/87	23:57	3

RUBIDOUX PAN DATA		
Date	Time /PST	PAN /ppbv
8/29/87	0:57	4
8/29/87	1:57	1
8/29/87	2:57	3
8/29/87	3:57	1
8/29/87	4:57	≤4
8/29/87	5:57	1
8/29/87	6:57	1
8/29/87	7:57	3
8/29/87	8:57	5
8/29/87	9:57	7
8/29/87	10:57	9
8/29/87	11:57	9
8/29/87	12:57	8
8/29/87	13:57	7
8/29/87	14:57	5
8/29/87	15:57	5
8/29/87	16:57	4
8/29/87	17:57	6
8/29/87	18:57	5
8/29/87	19:57	4
8/29/87	20:57	3
8/29/87	21:57	3
8/29/87	22:57	2
8/29/87	23:57	2
8/30/87	0:57	3
9/1/87	19:14	4
9/1/87	20:14	3
9/1/87	21:14	3
9/1/87	22:14	1
9/1/87	23:14	3
9/2/87	0:14	≤1
9/2/87	1:14	1
9/2/87	2:14	≤4
9/2/87	3:14	≤4
9/2/87	4:14	≤4
9/2/87	5:14	≤4
9/2/87	6:14	≤1
9/2/87	7:14	≤1
9/2/87	8:14	2
9/2/87	9:14	1
9/2/87	10:14	0
9/2/87	11:14	0
9/2/87	12:14	0

RUBIDOUX PAN DATA		
Date	Time /PST	PAN /ppbv
9/2/87	13:14	0
9/2/87	14:14	2
9/2/87	15:14	2
9/2/87	16:14	0
9/2/87	17:14	10
9/2/87	18:14	12
9/2/87	19:14	9
9/2/87	20:14	8
9/2/87	21:14	7
9/2/87	22:14	3
9/2/87	23:14	2
9/3/87	0:14	≤2
9/3/87	1:14	≤2
9/3/87	2:14	≤2
9/3/87	3:14	≤2
9/3/87	4:14	≤2
9/3/87	5:14	≤2
9/3/87	6:14	0
9/3/87	7:14	1
9/3/87	8:14	1
9/3/87	9:14	3
9/3/87	10:15	5
9/3/87	11:15	4
9/3/87	12:15	7
9/3/87	13:15	6
9/3/87	15:32	5
9/3/87	16:32	2
9/3/87	17:32	3
9/3/87	18:32	2
9/3/87	19:32	1
9/3/87	20:32	≤2
9/3/87	21:32	≤2
9/3/87	22:32	≤2
9/3/87	23:33	0

